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Certificate

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Patentanmeldung Nr. Patent application No. Demande de brevet n°

02102598.6

Der Präsident des Europäischen Patentamts;  
Im Auftrag

For the President of the European Patent Office

Le Président de l'Office européen des brevets  
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R C van Dijk

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**Blatt 2 der Bescheinigung**  
**Sheet 2 of the certificate**  
**Page 2 de l'attestation**

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Deformable colour photographic silver halide material

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## DESCRIPTION

## Field of the invention

5       The present invention relates to a deformable material for producing a deformed image without significant image degradation, said material has a good storage stability and is suitable for digital exposure with very short pixel times, large formats and automatic processing.

10

## Background of the invention.

Deformable materials with colour and/or black and white motives, particularly those made of plastic, are used e.g. as  
15 protective and/or decorative foils particularly in the furniture industry, in which they are used as design elements to cover low-priced and/or light weight carrier materials and/or carrier materials that are critical to the conditions of their use; the configuration of deformable material and carrier material replacing  
20 much more expensive and/or heavier and/or less easier to handle and/or less resistant materials such as real wood, stainless steel or marble.

The manufacture of deformed plastic pieces with any kind of representations like images, designs, patterns, letters and so  
25 forth, usually proceeds by printing on an undeformed flat foil of a thermoplastic polymer and is then deformed using heat and pressure.

The results obtained are unsatisfactory, because the printed pieces after deformation exhibit a loss in image quality, that is visible at all parts where the deformation has led to an elongation  
30 of the deformed material. In particular a significant loss in image quality is observed after deformation at curved parts and still more so at sharp edges, which is particularly noticeable as a bright line and/or increase granularity following the curves and/or edges in homogeneously coloured dark areas, which is unacceptable,  
35 particularly in the case of decorated furniture. Furthermore, the printing processes require complicated prepress steps and are therefore expensive and are not suitable for the manufacture of individual designs with small production runs.

Photographic layers, which were laminated onto a support,  
40 have, for example, been disclosed in EP-A 0 250 657, US 3,871,119, EP-A 0 490 416 and EP-A 0 276 506 for the manufacture of materials for identity cards and in EP-A 1 189 108 have been disclosed for

materials with a broader colour gamut. The layers can subsequently be covered with a protective foil, as disclosed, for example, in US 4,370,397 and GB 2,121,812.

The disclosed ID-cards are all flat, so that there are no requirements regarding deformability and their suitability or otherwise therefor was not disclosed.

Furthermore, as laminatable photographic layers those with special binders have been disclosed, although neither of these options produces an optimum image quality. In particular the graininess realized with state of the art laminatable materials is unacceptably high. The DTR materials that are also known to be laminatable, are not suitable for the furniture industry, because the two-sheet process has not been adapted to the large format automated processing needed in this field.

Representations like images, designs, patterns, letters and so forth, of the highest quality can be realized with colour photographic materials, comprising on a support at least one blue-sensitive silver halide emulsion layer containing at least one yellow coupler, at least one green-sensitive silver halide emulsion layer containing at least one magenta coupler and at least one red-sensitive silver halide emulsion layer containing at least one cyan coupler. As a support for reflective material, paper coated on both sides with polyethylene and for transparent materials longitudinally and laterally stretched polyester is usually used. The deformation according to the present invention of such colour photographic materials is not possible.

The deformability of special photographic materials consisting of a support, an optional adhesive layer and a black and white silver halide emulsion photographic layer with special binders was disclosed in FR 968 638 and GB 739,477. According to FR 968 638 gelatin cannot be used as a binder, because cracking occurred upon bending.

The known deformable photographic materials as disclosed in FR 968 638 and GB 739 477 did not fulfil the present quality requirements for photographically produced images and the bending behaviour was unsatisfactory.

GB 2,321,977 and the corresponding WO98/35269 disclose a mouldable photographic material comprising a thermoplastic base sheet, a primer layer providing a key for a light sensitive layer, and a protective thermoplastic foil, the foil being bonded to the light sensitive layer with an optical quality adhesive.

Furthermore, no deformable photographic materials are known, which are satisfactory for both a long exposure and for a digital exposure with very short pixel times, such as, for example, required in the furniture industry, to enable the exposure of large formats. 5 Analogue long exposures are desirable so that inexpensive exposure configurations can be used, but digital exposure is being increasingly required, because it is much faster and because rolls of film are much easier to expose continuously. Furthermore, different designs can be much more easily realized in production, 10 since no film is necessary as an intermediate step. Nowadays new designs are usually produced by computer and can be directly used in digital exposure to realize optimal image quality.

Digital exposure, also known as scanning exposure, proceeds pixel-wise, line-wise or area-wise with high intensity strongly 15 focussed beam of light beam e.g. from lasers, light emitting diodes (LED), DMD (digital micromirror devices) apparatuses, cathode ray tubes and such like and with short to very short exposure times per pixel. A pixel is the smallest image area on the copying material, which can be addressed by the exposure apparatus. Conventional 20 silver halide emulsions exhibit a too low sensitivity, due to an unsatisfactory reciprocity, which results in a too low contrast and insufficient maximum density at such short exposure times.

A similar reciprocity failure is also observed at exposure times above 10 s (long exposure times), which are necessary for 25 analogue exposure of large formats.

Furthermore, the known deformable photographic materials are unsatisfactory with regard to the storage stability of the unexposed and unprocessed materials, in particular when the support of the photographic material contains additives like plastizisers, 30 stabilizers, and so forth.

Objects of the invention.

It is therefore an object of the present invention to provide 35 a deformable colour photographic material, which enables high quality representations like images, designs, patterns, letters and so forth to be realized, which undergo the desired deformation by heat and/or pressure without significant visible loss in image quality. A further advantage of the present invention compared to 40 printing processes is the possibility to produce even single pieces as a proof or demonstration example.

Further aspects and advantages of the invention will become apparent from the description hereinafter.

#### Summary of the invention

5

It has been surprisingly found, that the deformable colour photographic recording material of the present invention is suitable for digital exposure even at pixel times lower than 200 ns, exhibits a very good storage stability of the unexposed and  
10 unprocessed material and gives high quality images, said colour photographic silver halide material comprising on a deformable plastic support at least one blue-sensitive silver halide emulsion layer containing at least one yellow coupler, at least one green-sensitive silver halide emulsion layer containing at least one  
15 magenta coupler and at least one red-sensitive silver halide emulsion layer containing at least one cyan coupler, wherein the silver halide emulsions have an overall silver chloride content of at least 95 mol% and at least one silver halide emulsion contains silver halide crystals that are doped with 10 to 700 nmol,  
20 preferably 10 to 500 nmol Ir.

Surprisingly it has been found, at variance with the disclosure in FR 968 638, that gelatin can be successfully used in the materials used in the process according to the present invention. The reason why the use of gelatin failed according to FR  
25 968 638, but surprisingly was very successful for the present invention, may be the difference between single layer black and white materials like those described in FR 968 638, that essentially only contain silver halide crystals dispersed in the binder, and multilayer colour photographic materials according to  
30 the present invention, that also comprise softer materials like couplers in their layers.

Aspects of the present invention are realized with a deformable colour photographic silver halide material, the colour photographic silver halide material comprising on a deformable  
35 plastic support at least one blue-sensitive silver halide emulsion layer containing at least one yellow coupler, at least one green-sensitive silver halide emulsion layer containing at least one magenta coupler and at least one red-sensitive silver halide emulsion layer containing at least one cyan coupler, wherein the  
40 silver halide emulsions have an overall silver chloride content of at least 95 mol% and at least one silver halide emulsion contains silver halide crystals that are doped with 10 to 700 nmol iridium.



Aspects of the present invention are also realized with a process for producing a deformed image comprising the steps of: exposing the above-mentioned colour photographic silver halide material, preferably digitally; conventionally processing the exposed colour photographic material to produce an image; and deforming the colour photographic material.

Detailed description of the invention.

10

#### Definitions

The term deformation (also known as moulding) used in disclosing the present invention refers to three-dimensional deformation in which an initially flat object e.g. a plate or a sheet is deformed to a three dimensional shape using a shaping tool to which pressure and/or heat is applied, in the course of which at least a part of the initially flat object is elongated (stretched), the shape being maintained upon cooling and/or upon releasing the pressure. The out-of-plane deformation is usually of a greater measure than the thickness of the initially flat object, the thickness being defined as the distance between the surface to which the tool is applied and the opposite surface of the initially flat object.

The term to deform means the process of deformation.

25 The term deformable plastic as used in disclosing the present invention includes all polymers, which can be deformed, without fracturing, exhibiting cracks or thermally decomposing. The term deformable plastic includes all polymers, that are available in foil form and that are not stretched..

30 The term conventional processing as used in disclosing the present invention means chromogenic chemical colour processing as used for the processing of conventional photographic materials such as color papers, color films or display materials and is further specified in the following description.

35 The terms immediate and fast hardeners mean that the hardener is capable of hardening gelatin immediately after coating or at least several days after coating to such an extent that no further changes in sensitometry and swelling behaviour due to the presence of hardener occur. By swelling is meant the difference between wet layer thickness and dry layer thickness upon aqueous processing of the material.

40

The term silver nitrate (equivalent to AgX present) is used in the examples to characterize the silver halide emulsions means the weight of silver nitrate in a given amount of silver halide emulsion that results when the quantity of silver halide in the  
5 emulsion is hypothetically converted into the equivalent weight of silver nitrate.

#### Process for producing a deformed image

10 Aspects of the present invention are also realized with a process for producing a deformed image comprising the steps of: exposing the above-mentioned colour photographic silver halide material, according to the present invention, preferably digitally; conventionally processing the exposed colour photographic material  
15 to produce an image; and deforming the colour photographic material. There are commonly used apparatus available for exposure and conventional processing of the photographic material of the present inventions that are able to process long and wide sheets as well as wide rolls of the material as are needed e.g. in  
20 the furniture industry.

Exposure preferably is carried out digitally and proceeds preferably from the side remote from the support, but in the case of a transparent or slightly coloured support exposure can also be carried out through the support if a loss in sharpness is  
25 tolerable.

To avoid light scattering and resulting loss in sharpness in the case of a transparent or translucent support, it is preferred to place a dark sheet in contact with the side of the material remote from the light source upon exposure. The same effect can be  
30 achieved when the material comprises an antihalation layer, that is bleached during the chemical processing of the material. Suitable absorbing material for said antihalation layer is described in Research Disclosure 38 957, 1996, VIII., from page 610, herein incorporated by reference. The antihalation layer has to be  
35 arranged on the side of the emulsion layers remote from the light source.

In a preferred embodiment of the deformable colour photographic silver halide material, according to the present invention, the support is provided on the image side between the  
40 silver halide layers and the support with a layer reflecting white light and on the opposite side with a non-bleachable black

antihalation layer as described in US 4 224 402, herein incorporated by reference.

After image-wise exposure the colour photographic material is appropriately processed. Details of processing and the chemicals required therefor together with exemplary colour photographic materials are to be found in Research Disclosure 37254, part 10 (1995) page 294 and in Research Disclosure 37038, parts XVI to XXIII (1995), from page 95, herein incorporated by reference. Conventional processing of the colour photographic material comprises the steps of chromogenic development, bleaching and fixing and for colour reversal materials in addition a reversal step and a black and white development. The bleaching and fixing steps can be carried out within one bleach/fixing step. Processes and the compounds especially suitable for the process of the present invention are commonly known in the art and described e.g. in Ullmann's Encyclopedia of Industrial Chemistry, 5<sup>th</sup> edition, Vol. A20, p 68 to 98, herein incorporated by reference, in particular the color negative paper processes such as EP-2 (Eastman Kodak) and AP 92 (Agfa) for silver bromide chloride emulsions and RA-4 (Eastman Kodak) and AP 94 (Agfa) processes for predominantly silver chloride emulsions.

In another preferred embodiment of the process, according to the present invention, the conventional processing of the colour photographic material is carried out with development times between 15 and 130 s. Longer development times are necessary, if, for example, silver-rich materials are processed in order to attain a particularly high colour density.

#### Deformable plastic support

30

Deformable plastics are those which can be deformed, without fracturing, exhibiting cracks or thermally decomposing. All polymers, that are available in foil form and that are not stretched fall under the term deformable plastics.

35

A good reference point for the temperature necessary for deformation is the glass transition temperature (T<sub>g</sub>). Deformation is usually done between the glass transition temperature and the melting point of the deformable plastic. The pressure needed for deformation can easily be tested; the higher the deformation temperature is with respect to the glass transition temperature, the lower the pressure needed. Just below the melting point only a very low pressure is needed. The time needed for the deformation

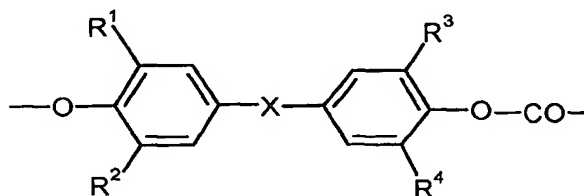
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can also be easily tested and adjusted. A higher temperature and/or a higher pressure results in a shorter time.

Suitable support materials, e.g. foils, films or sheets, are preferably taken from the group of plastics known as thermoplastics and include poly(vinylchloride) (PVC), polycarbonate (PC), non-oriented polyester, acrylonitrile-butadiene-styrene (ABS), polyolefin, copolymers and mixtures of said polymers. Suitable copolymers include vinylchloride copolymer, in particular ABS copolymerized with vinylchloride and polyolefin copolymer.

10 According to a preferred embodiment of the deformable colour photographic silver halide material, according to the present invention, deformable plastic support is a polycarbonate, poly(vinylchloride), vinylchloride copolymer or a polyester; or a copolyester based on PET.

15 Suitable polycarbonates for use in the colour photographic material of the present invention, contain repeating units represented by the formula



20

wherein X represents  $\text{—S—}$ ,  $\text{—SO}_2\text{—}$ ,  $\text{—C(R}_5, \text{R}_6)\text{—}$  or  $\text{—C[=C(R}_7, \text{R}_8)]\text{—}$ ;  $\text{R}_1$ ,  $\text{R}_2$ ,  $\text{R}_3$ ,  $\text{R}_4$ ,  $\text{R}_7$  and  $\text{R}_8$  independently represent a hydrogen atom, or an alkyl- or aryl- group; and  $\text{R}_5$  and  $\text{R}_6$  independently represent a hydrogen atom or an alkyl- or aryl- group or together represent the atoms necessary to form a cycloaliphatic ring, e.g. a cyclohexane ring. The polycarbonates preferably have weight averaged molecular weights between 10,000 and 500,000. Polycarbonates based on bisphenol A are particularly preferred. Poly(vinylchloride) for use in the colour photographic material of the present invention, preferably contain at least 50% by weight vinylchloride units and optionally contain further hydrophobic units. Preferred comonomers are vinylidene chloride, vinyl acetate, acrylonitrile, styrene, butadiene, chloroprene, dichlorobutadiene, vinyl fluoride, vinylidene fluoride and 35 trifluoroethylene.

The poly(vinylchloride) preferably contains 60 to 65% by weight of chlorine. A PVC support used in the colour photographic

material of the present invention, can contain plasticizers, but for ecological reasons and for reasons of stability of the photographic material preferably contains no plasticizers.

Furthermore, the PVC can contain stabilizers and antioxidants with  
5 inorganic heavy metal salts, metal soaps (particularly of Ba, Cd, Pb, Zn and Ca), dibutyl and dioctyl tin compounds and epoxidized soya oil. Further optional ingredients of PVC include lubricants, impact modifier, process aids, fillers, fire retardants, smoke repressants, blowing agents, colourants, antistatic agents,  
10 viscosity modifier, biostabilizers and UV absorber.

Suitable polyesters include condensation products of aromatic, aliphatic or cycloaliphatic dicarboxylic acids with aliphatic or alicyclic glycols, whereby the dicarboxylic acids have preferably 4 to 20 C-atoms and the glycols preferably 2 to 24 C-atoms. The  
15 polyesters can also be modified by adding small quantities of other monomers. Preferred polyesters are poly(ethylene terephthalate) (PET) or copolyesters based on PET (CoPET) such as the preferred CoPET Eastar PETG Copolyester 6763 delivered by Eastman (PETG). However, stretched (oriented) polyesters are unsuitable, because  
20 they form micro-cracks upon deformation.

Suitable polyolefins include polypropylene, polyethylene and polymethylpentene either individually or as mixtures. Preferred polyolefins include copolymers of propylene and/or ethylene with hexene and/or butene and/or octene.

25 Preferred deformable plastics for deformable colour photographic materials, according to the present invention, are PVC, vinylchloride copolymer and PC, because they bend well and the photographic layer is particularly little affected. PC is particularly preferred due to its high tensile strength and ensures  
30 a good storage stability.

The support can be a single layer foil, but can also consist of a compound arrangement of several plastic foils. All plastic foils must be of a deformable plastic. The thickness of the support is preferably between 0.05 and 0.75 mm.

35 The support can be coated with one or several layers to provide the support with e.g. a colour layer or an adhesive layer.

Depending upon the desired effect, the support can be white, transparent, translucent or coloured with dyes or pigments and may also have structure or roughness on either or both sides.

40 Structure or roughness in the foil is preferably realized during its manufacture.

The support may contain pigments or other colorants. An opaque, white colour can be realized by coextrusion of white pigments such as titanium dioxide. Suitable colorants include dyes such as Ultramarine Blue.

5 To improve the adhesion of hydrophilic layers of colour photographic materials on hydrophobic supports, it is preferred to pretreat the support with a hydrophilizing process, for example corona (air ionization at about 10 to 20 kV) treatment. Furthermore, a subbing layer between the support and the layer of  
10 the layer configuration of the colour photographic material closest to the support is also preferred.

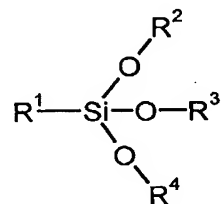
In a preferred embodiment of the deformable colour photographic silver halide material, according to the present invention, the deformable colour photographic material further  
15 contains a subbing layer containing 1.3 to 80% by weight of a proteinaceous colloid, 0 to 85% by weight of colloidal silica and 0 to 30% by weight of a siloxane, which can form a reaction product with the colloidal silica. In a further preferred embodiment of the deformable colour photographic silver halide material,  
20 according to the present invention, the deformable colour photographic material, further contains a subbing layer on the same side of the support as the silver halide emulsion layers. Particularly preferred is a subbing layer that further contains 1.0 to 70% by weight of an ionogenic polyester-polyurethane, which is  
25 coated from an aqueous dispersion, in which isocyanate groups in its structure have reacted with an ionomer compound, which contains at least one active hydrogen atom and a carboxylate or sulphonate salt group, and in which the number of salt groups is sufficiently high to render the polyester-polyurethane dispersible in an aqueous  
30 medium. Preferred proteinaceous colloids are gelatin and casein, with gelatin being particularly preferred. Suitable anionic polyester-polyurethanes are disclosed in US 3,397,989, US 4,388,403 and DE-OS 3 630 045, herein incorporated by reference, with those with carboxylate and sulphonate groups, such as disclosed in US  
35 3,397,989, being particularly preferred. The polyester-polyurethanes preferably contain a linear polyester with OH-end groups and a molecular weight between 300 and 2,000. The polyester-polyurethanes are preferably employed as an aqueous dispersion, with a particularly preferred dispersion containing the  
40 reaction products of the following components with respect to the end dispersion: 23% by weight of a polyester based on adipic acid and hexandiol with an average molecular weight of 840, 14% by

weight 4,4'-diisocyanatodicyclohexylmethane, 2% by weight dimethylolpropionic acid and 1.5% by weight of trimethylamin, with the composition further containing 7.5% by weight N-Methyl-pyrrolidon and 52% by weight water. Said particularly preferred dispersion is called hereinafter dispersion (D-1).

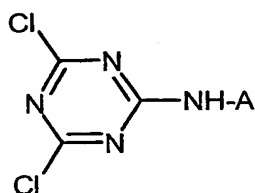
Suitable polyester-polyurethane dispersions include Dispercoll® products from BAYER.

Suitable colloidal silica's include products marketed under the trade names LUDOX® (Du Pont), SYTON® (Du Pont) and KIESELSOLE® (Bayer). Their average particle size is preferably between 5 and 100 nm.

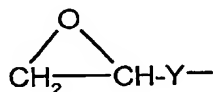
Suitable siloxanes are represented by the formula:



in which R<sup>1</sup> represents a polymerizable group or has a OH- and/or NH<sub>2</sub>- group which can react with the protein-containing colloid, particularly a group which contains a reactive halogen, an epoxy group or an α, β-ethylenically unsaturated group. Examples of R<sup>1</sup> are: ClCH<sub>2</sub>CONH-A-; BrCH<sub>2</sub>CONH-A-; CH<sub>2</sub>=CH(CH<sub>3</sub>)COO-A-; CH<sub>2</sub>=CHSO<sub>2</sub>CH<sub>2</sub>OCH<sub>2</sub>SO<sub>2</sub>NH-A-; CH<sub>2</sub>=CHCONH-A-; CH<sub>2</sub>=C(CH<sub>3</sub>)CONH-A-;



in which A represents an alkylene group, or

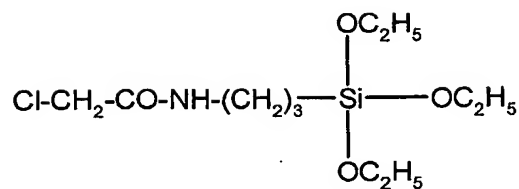


and in which Y represents a bivalent hydrocarbon chain, which can be interrupted by oxygen. R<sup>2</sup>, R<sup>3</sup> and R<sup>4</sup> independently represent an optionally substituted hydrocarbon group such as methyl or ethyl.

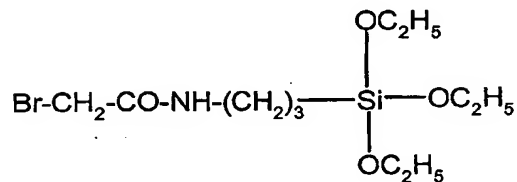
Suitable siloxane compounds include:

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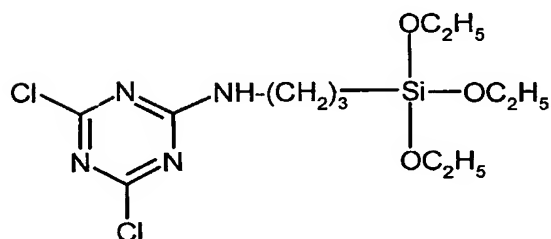
SL-1



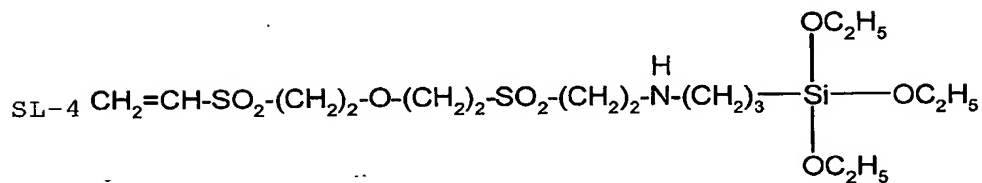
SL-2



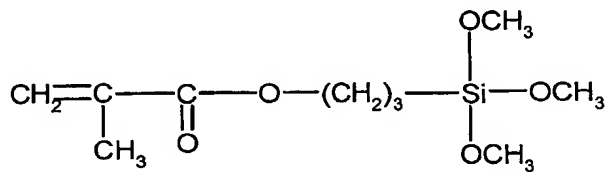
SL-3



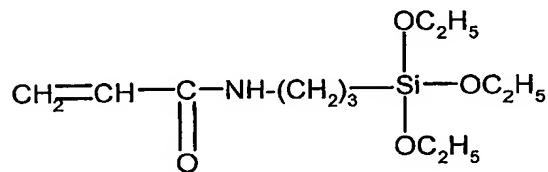
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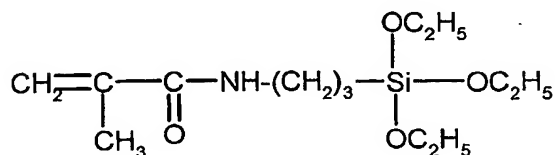


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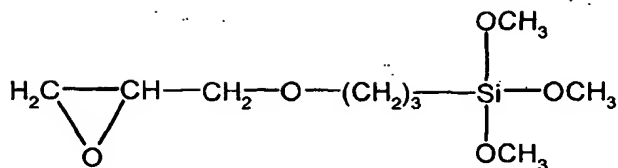


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SL-7







Suitable wetting agents include those containing saponines and products marketed under the trade names TERGITOL® (supplied by Union Carbide Corp. and Niacet Corp.) or Manoxol® (supplied by e.g. Rohm and Haas).

In a further preferred embodiment of the deformable colour photographic silver halide material, according to the present invention, the deformable plastic support is laminatable e.g. by coating the backside of the support with an adhesive layer suitable for pressure and/or heat adhesion processes. Such pressure sensitive adhesive layers are preferably covered with a protective foil. The adhesive layer, with or without protective foil, can be applied to the support at any time before lamination, thus even before the coating of the support with light-sensitive layers. It is preferred to apply the adhesive layer after processing the colour photographic material.

25 Provision of a protective foil on the outermost layer of the image  
side of the support

In a preferred embodiment of the deformable colour photographic silver halide material, according to the present invention, the outermost on the image side of the deformable colour photographic material is provided with a protective foil, preferably via an adhesive layer, which, for example, protects the image from scratching and environmental effects due to oxygen, UV-light and water. The protective foil provided on the image side of the support preferably comprises homopolymers such as PVC, PC, a polyalkylene or a polyester such as PET or CoPET, in particular PVC. The protective foil can also comprise block copolymers with polymer subunits that are preferably selected from the

aforementioned homopolymers; mixed copolymers obtained by mixed polymerization of at least two monomers, in particular of at least two different vinyl monomers such as a vinylchloride, an alkylene or a styrene; or blends of at least two polymers selected from the  
5 aforementioned homopolymers and/or block copolymers and / or mixed copolymers.

In a preferred embodiment of the present invention, the adhesive layer is a polyalkylene foil (adhesive foil), in  
10 particular a polyethylene foil, that can be laminated in direct contact to the protective foil or that is adhered to the protective foil using a glue layer.

Preferably the protective foil and/or the adhesive layer and/or the glue layer if present contain a UV-absorber such as  
15 hydroxybenzophenone or hydroxybenzotriazole. Preferred UV-absorber are those known under the trade name Tinuvin and are delivered by Ciba-Geigy. Suitable protective foils, adhesives and glues include those disclosed in EP-A 0 348 310, US 4,456,667, US 4,455,359, US 4,378,392, US 4,370,397, US 3,871,119 and GB-A 2,321,977 herein  
20 incorporated by reference. The protective foil can consist of a single polymer composition or can be a mixture or a laminate of the same or different polymers, taken from the group of PVC, PC, PET, CoPET or a polyalkylene. It is preferred, that at least one of the polymers used for the protective foil is of the same plastic  
25 material that is used for the support.

In a preferred embodiment of the protective foil used for the material, according to the present invention, the protective foil has a  $T_g$  that is similar to the  $T_g$  of the deformable plastic support. Particularly preferred adhesive foils of polyethylene  
30 have a melting point of ca. 90 to 100°C.

In a further preferred embodiment of the protective foil used for the material, according to the present invention, the protective foil can be coloured and/or printed with any kind of design, image or text.

35 The sandwich of protective foil, optionally a glue layer and the adhesive layer is preferably laminated to the image side of the photographic material using a roller laminator.

According to a preferred embodiment of the process, according to the present invention, the deformable colour photographic silver  
40 halide material is provided with a protective foil before deforming the colour photographic material with a work piece.

### Deformation of the colour photographic material

The deformation of the colour photographic material usually is carried out after conventional processing of the exposed colour photographic material, but can also be done before processing and even before exposure. However, it is preferred to carry out the deformation after conventional processing of the exposed colour photographic material.

According to a preferred embodiment of the process, according to the present invention, the deforming step comprising the application of heat and pressure and wherein at least part of the deformable colour photographic material is elongated during the process. The tool used in the deformation step can, for example, be a mould into which the heated plastic is sucked, blown or pressed. In the furniture industry, for example, the piece of furniture to which the colour photographic material is to be applied, can itself be the shaping tool. In this case the shaping tool is termed the "work piece". The colour photographic material is thereby pressed onto the piece of furniture (the work piece), for example with the aid of a membrane press, and thereby intimately attached to the piece of furniture. In this process the work piece covered with the photographic material is pressed onto an elastic membrane (usually made of rubber) which itself is placed on top of a tank completely filled with hot water of about 95°C or filled with hot oil to enable the process, according to the present invention, to be carried out at higher temperatures.

According to a preferred embodiment of the process, according to the present invention, the deforming step comprises deforming the deformable colour photographic material by vacuum deformation.

Adhesion of the deformed colour photographic material to the piece of furniture is preferably supplemented with an adhesive. In the case of very soft materials deformable at room temperature (25°C) a pressure adhesive is sufficient (e.g. a contact adhesive). The piece of furniture, e.g. a piece of chipwood, has only been taken as an example. The deformable colour photographic material, according to the present invention, can easily be used in other technical areas, e.g. the automotive industry, by just replacing the work piece and using adhesives that are known to work for the material the work piece is made of.

According to a preferred embodiment of the process, according to the present invention, the deforming step comprises deforming

the deformable colour photographic material by injection moulding, wherein the photographic material is placed in a die mould and the injected plastic material deforms the photographic material and forms a single entity with the deformable colour photographic material.

In a preferred embodiment of the process, according to the present invention, the deforming step comprises deforming the deformable colour photographic material in contact with a work piece

Usually the support side of the deformable colour photographic material is applied to the work piece e.g. a piece of furniture. In this case it is preferable that the image side of the processed colour photographic material is provided with a transparent protective foil as described above just before the deformation step so as to prevent damage during the deformation step.

If the support is clear or at least transparent and not too strongly coloured, the silver halide emulsion-side of the deformable colour photographic material can be applied to the work piece. In such cases, in addition to the usual cold and hot-melt adhesives, a gelatin solution containing a gelatin-hardening agent can also be used as an adhesive. Instead of adhering the silver halide emulsion-side directly to the work piece, a preferably reflective, e.g. white or opaque protective foil can be placed in between the silver halide emulsion side of the colour photographic material and the work piece.

In a preferred embodiment of the present invention, the adhesion of the deformed photographic material to the work piece is further improved, particularly at the corners and edges of the work piece and where the deformed material ends, e. g. at the corners and the edges on the back side of a piece of furniture. This can be carried out by pretreatment of the work piece, particularly at the corners and edges, with a glue before the deformation; or processing the work piece coated with the deformable photographic material with a hot-knife and/or applying glue after deformation and if necessary after having cut-off surplus photographic material to seal the corners and edges and to prevent peeling of the deformed material.

#### Colour photographic material

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In a preferred embodiment of the present invention, the silver halide emulsions have an overall silver chloride content of at

least 98 mol%. Silver halide emulsions which are substantially free from silver iodide are preferred, emulsions with less than 1 mol% iodide and in particular emulsions with less than 0.1 mol% iodide being particularly preferred.

5 At least one silver halide emulsion used in the material, according to the present invention, preferably contains silver halide crystals that are doped with at least one dopant alone or in addition to Ir. For silver halide crystals with a high silver chloride content the preferred dopants in addition to Ir are Rh-  
10 and Hg-salts.

It is particularly preferred, that at least one blue-, at least one green- and at least one red-sensitive silver halide emulsion layer in each case comprises at least one silver halide emulsion whose silver halide crystals are doped with at least 10 to  
15 700 nmol, preferably 10 to 500 nmol Ir.

Preferably the silver halide crystals are doped with Ir in form of Ir(IV)-salts or complexes, particularly with salts or complexes comprising halide ions such as chloride or fluoride, acetate ions, or ligands such as nitrosyl or 5-methyl thiazole.

20 Suitable dopants for the emulsions used in the material of the present invention and processes for the addition of said dopants are to be found in Research Disclosure 37038, parts XV-B (1995); from page 90 herein incorporated by reference.

The silver halide emulsions used in the colour photographic  
25 material of the present invention, can be prepared by a simple double jet process, a double jet process with separate preprecipitation (formation of crystal nuclei) and precipitation thereon or a combined double jet recrystallization process. In a preferred embodiment of the material according to the present  
30 invention, the preparation of at least one silver halide emulsion used for the material comprises the recrystallization of a Lippmann (mikrate) emulsion.

In a preferred embodiment, according to the present invention, the Ir dopants are added to the halide solution, when preparing the  
35 emulsions by a simple double jet process and added to the Lippmann emulsion, when a Lippmann emulsion (mikrate) recrystallization process is used.

At least one silver halide emulsion preferably contains silver halide crystals with at least two different zones (structured  
40 crystals), in which the outermost zone has a higher molar content of silver bromide than the rest of the crystal. The nucleus of the structured crystals is preferably prepared by a double jet process

with a silver nitrate solution and a halide solution, predominantly chloride, and precipitation thereon preferably occurs by recrystallization of a fine-grained silver bromide-chloride emulsion (Lippmann emulsion) with a molar silver bromide content of  
5 at least 5 percent.

According to a preferred embodiment of the deformable colour photographic silver halide material, according to the present invention, at least one silver halide emulsion contains structured crystals with at least two different zones, the outermost zone  
10 having a higher molar content of silver bromide than the rest of the crystal.

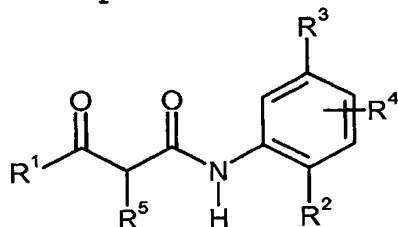
According to another preferred embodiment of the deformable colour photographic silver halide material, according to the present invention, at least one blue-, at least one green- and at  
15 least one red-sensitive silver halide emulsion layer in each case comprises at least one silver halide emulsion which contains the structured crystals.

According to another preferred embodiment of the deformable colour photographic silver halide material, according to the present invention, the green-sensitive silver halide emulsion layer  
20 and/or the red-sensitive silver halide emulsion layer contains at least one silver halide emulsion with silver halide crystals having an average grain size (volume averaged, diameter of a sphere with an equivalent volume) of at least 0.40  $\mu\text{m}$ .

According to another preferred embodiment of the deformable colour photographic silver halide material, according to the present invention, the silver halide emulsions contain one or more  
25 binders, with the binders being at least 80% by weight of gelatin being particularly preferred.

30 In a preferred embodiment of the colour photographic material, according to the present invention, yellow couplers, purple couplers and blue-green couplers represented by formulae (IV), (V), (VI), (XIV), (VII) and (VIII) are used.

**Yellow coupler:**

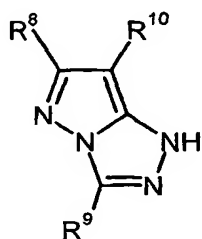


(IV)

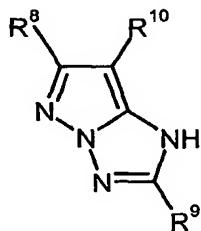
35 wherein

- $R^1$  represents alkyl, alkoxy, aryl or hetero-aryl groups,  
 $R^2$  represents alkoxy or aryloxy groups or halogen,  
 $R^3$  represents  $-CO_2R^6$ ,  $-CONR^6R^7$ ,  $-NHCO_2R^6$ ,  $-NHSO_2-R^6$ ,  $-SO_2NR^6R^7$ ,  
 $-SO_2NHCOR^6$ ,  $-NHCOR^6$  groups, Cl  
 $R^4$  represents hydrogen or a substituent,  
 $R^5$  represents hydrogen or a group which can be split off during  
coupling,  
 $R^6$ ,  $R^7$  independently represent hydrogen or alkyl or aryl groups and  
one of the  $R^2$ ,  $R^3$  and  $R_4$  group is a ballast group.

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**Magenta coupler:**

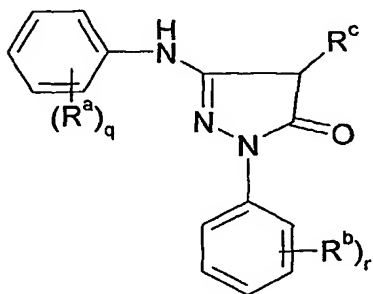
(V);



(VI);

wherein

- $R^8$  and  $R^9$  independently represent hydrogen or alkyl, aralkyl, aryl,  
 $R^8$  and  $R^9$  independently represent hydrogen or alkyl, aralkyl, aryl,  
aryloxy, alkylthio, arylthio, amino, anilino, acylamino,  
cyano, alkoxycarbonyl, alkylcarbonyl or alkylsulfamoyl  
groups, wherein these groups are optionally further  
substituted and wherein at least one of these groups contains  
a ballast group, and  
 $R^{10}$  represents hydrogen or a group which can split off during  
chromogenic coupling.  
 $R^8$  is preferably a tert.-butyl group;  $R^{10}$  is preferably chlorine.



(XIV)

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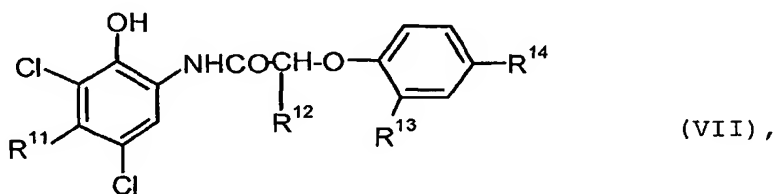
wherein  $r$  is an integer from 1 to 5;  $q$  is 1, 2 or 3;  $R^c$  represents a  
group which can split off during chromogenic coupling;  $R^a$   
represents halogen or alkoxy or acylamino groups; and  $R^b$  represents

halogen or cyano, thiocyanato, alkoxy, alkyl, acylamino or alkoxy carbamyl groups.

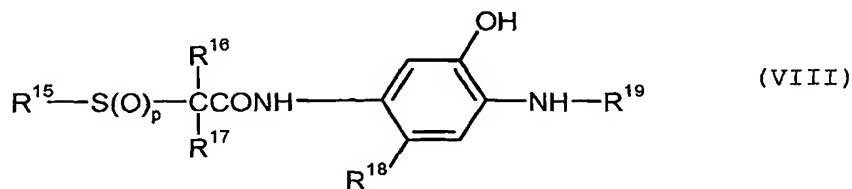
R<sup>c</sup> is preferably hydrogen or a group which can split off as an anion under the basic conditions of chromogenic coupling.

Particularly preferred, R<sup>c</sup> represents -S-aryl or -N=N-aryl, wherein aryl preferably is a phenyl or naphthyl group, that is optionally substituted by halogen, like chlorine or bromine or C<sub>1</sub>-C<sub>18</sub>-alkyl or C<sub>1</sub>-C<sub>18</sub>-alkoxy groups.

**Cyan coupler:**



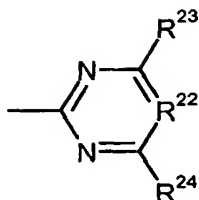
wherein R<sup>11</sup>, R<sup>12</sup>, R<sup>13</sup> and R<sup>14</sup> independently represent hydrogen or a C<sub>1</sub>-C<sub>6</sub>-alkyl group. R<sup>11</sup> is preferably a CH<sub>3</sub> or C<sub>2</sub>H<sub>5</sub>; R<sup>12</sup> is preferably a C<sub>2</sub>-C<sub>6</sub>-alkyl group; and R<sup>13</sup> and R<sup>14</sup> are preferably t-C<sub>4</sub>H<sub>9</sub> or t-C<sub>5</sub>H<sub>11</sub>.



wherein R<sup>15</sup> represents alkyl, alkenyl, aryl or hetero-aryl groups; R<sup>16</sup>, R<sup>17</sup> independently represent hydrogen, alkyl, alkenyl, aryl or hetero-aryl groups; R<sup>18</sup> represents hydrogen or a group which can split off during chromogenic coupling; R<sup>19</sup> represents -COR<sup>20</sup>, -CO<sub>2</sub>R<sup>20</sup>, -CONR<sup>20</sup>R<sup>21</sup>, -SO<sub>2</sub>R<sup>20</sup>, -SO<sub>2</sub>NR<sup>20</sup>R<sup>21</sup>, -CO-CO<sub>2</sub>R<sup>20</sup>, -COCONR<sup>20</sup>R<sup>21</sup> or a group with the formula



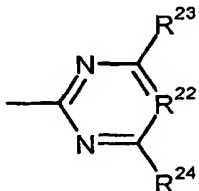
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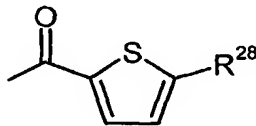
wherein  $R^{20}$  represents alkyl, alkenyl, aryl or hetero-aryl groups;  
 $R^{21}$  represents hydrogen or  $R^{20}$ ;  $R^{22}$  represents  $-N=$  or  $-C(R^{25})=$ ;  $R^{23}$ ,  
 $R^{24}$  and  $R^{25}$  independently represent  $-OR^{21}$ ,  $-SR^{21}$ ,  $-NR^{20}R^{21}$ ,  $-R^{21}$  or  
 5 Cl; and  $p$  is 1 or 2.

The following groups of couplers according to formula (VIII)  
 are preferred:

- (1) couplers in which  $p = 1$  and  $R^{15}$  to  $R^{25}$  have the meaning given  
 above.
- 10 (2) couplers in which  $p = 2$ ,  $R^{19}$  represents  $-CO-R^{26}$ ,  $R^{26}$  represents  
 alkenyl or hetero-aryl groups and  $R^{15}$  to  $R^{18}$  have the meanings  
 given above.
- (3) couplers in which  $p = 2$ ,  $R^{19}$  represents  $-SO_2R^{27}$ ,  $-SO_2N(R^{27})_2$ ,  
 $-CO_2R^{27}$ ,  $-COCO_2-R^{27}$ , or  $-COCO-N(R^{27})_2$ ,  $R^{27}$  represents alkyl,  
 15 aryl, alkenyl or hetero-aryl groups and  $R^{15}$  to  $R^{18}$  have the  
 meanings given above.
- (4) couplers in which  $p = 2$ ,  $R^{19}$  represents a group with the  
 formula

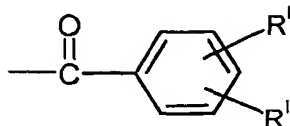


- 20 and  $R^{15}$  to  $R^{18}$  and  $R^{22}$  to  $R^{24}$  have the meanings given above.
- (5) couplers in which  $p = 2$  and  $R^{19}$  represents a group with the  
 formula



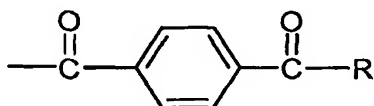
- 25  $R^{28}$  represents hydrogen, Cl, CN, Br, F,  $-COR^{29}$ ,  $-CONHR^{29}$  or  
 $CO_2R^{29}$  and  $R^{29}$  represents alkyl or aryl groups.
- (6) couplers in which  $p = 2$  and  $R^{19}$  represents a group with the  
 formula

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wherein  $R^I$  represents halogen, CN,  $-CF_3$  or alkoxy carbonyl groups;  $R^{II}$  represents hydrogen or has the same meaning as  $R^I$ ; and  $R^{15}$  to  $R^{18}$  have the meanings given above.

- (7) couplers in which  $p = 2$  and  $R^{19}$  represents  $-COR^{20}$ ;  $R^{20}$  represents alkyl, aryl or hetero-aryl groups and  $R^{15}$  to  $R^{18}$  have the meanings given above.
- (8) couplers in which  $p = 2$  and  $R^{19}$  represents a group with the formula

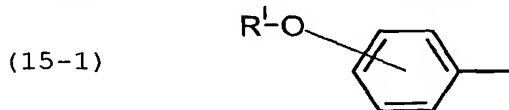


wherein  $R^I$  represents  $-OR^{II}$  or  $-NR^{III}R^{IV}$ ;  $R^{II}$  and  $R^{III}$  represent an optionally substituted  $C_1-C_6$ -alkyl group;  $R^{IV}$  represents hydrogen or has the same meaning as  $R^{III}$ ; and  $R^{15}$  to  $R^{18}$  have the meanings given above.

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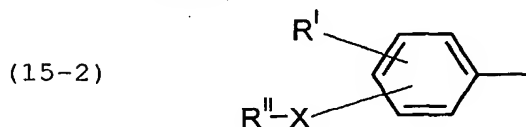
In the formula (VIII) and the Compounds (1) to (8) the substituents have the following preferred meanings:  $R^{15}$  represents alkyl or aryl groups;  $R^{16}$  and  $R^{17}$  independently represent H or alkyl or aryl groups;  $R^{18}$  represents H, Cl, alkoxy, aryloxy, alkylthio or arylthio groups;  $R^{22}$  represents  $-N=$ ; and  $R^{23}$  and  $R^{24}$  independently represent  $-OR^{21}$ ,  $-NR^{20}R^{21}$  or  $-Cl$ .

In formula (VIII) and the Compounds (1) to (8) the substituents have the following particularly preferred meanings:  $R^{15}$  is a group according to one of formulae (15-1), (15-2) and (15-3):



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wherein  $R^I$  represents an alkyl group with at least 8 C-atoms;

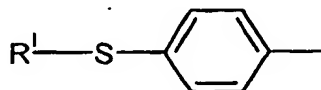


wherein  $R^I$  represents alkyl, alkenyl, alkoxy, aryloxy, acyloxy, acylamino, sulfonyloxy, sulfamoylamino, sulfonamido, ureido, hydroxycarbonyl, hydroxy,

30

carbonylamino, carbamoyl, alkylthio, arylthio, alkylamino, arylamino groups or hydrogen;  $R^{II}$  represents an alkyl or aryl group; X represents S, NH or  $NR^{III}$  and  $R^{III}$  represents an alkyl or aryl group;

(15-3)



5

wherein  $R^I$  represents an optionally substituted alkyl group;

$R^{16}$  represents an alkyl group, in particular  $C_1$ - $C_4$ -alkyl group;  $R^{17}$  represents H; and  $R^{20}$  represents an alkyl or aryl group.

Particularly preferred couplers are group (6) couplers according to formula (VIII) in which  $R^{15}$  is represented by formula (15-1); group (7) couplers according to formula (VIII) in which  $R^{15}$  is represented by formula (15-2); group (8) couplers according to formula (VIII) in which  $R^{15}$  is represented by formula (15-3); and group (8) couplers according to formula (VIII) and  $R^{15}$  is a group with 8 to 18 carbon atoms.

Alkyl- and alkenyl- groups can be straight chain, branched, cyclic and optionally substituted. Aryl- and hetero-aryl- groups are optionally substituted and the aryl group is preferably a phenyl group. Possible substituents for the alkyl, alkenyl, aryl and hetero-aryl groups are: alkyl, alkenyl, aryl, hetero-aryl, alkoxy, aryloxy, alkenyloxy, hydroxy, alkylthio, arylthio, halogen, cyano, acyl, acyloxy or acylamino groups, wherein an acyl group can be derived from an aliphatic, olefinic or aromatic carbonic, carboxylic, carboxylamino, sulfonic, sulfonamido, sulfinic, phosphoric, phosphonic or phosphorous acid.

Examples of cyan couplers according to formula (VII) are:

VII-1 with  $R^{11} = C_2H_5$ ,  $R^{12} = n-C_4H_9$ ,  $R^{13} = R^{14} = t-C_4H_9$ ,

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VII-2 with  $R^{11} = R^{12} = C_2H_5$ ,  $R^{13} = R^{14} = t-C_5H_{11}$ ,

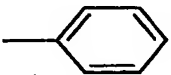
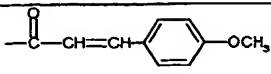
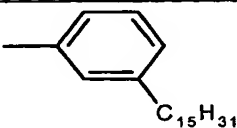
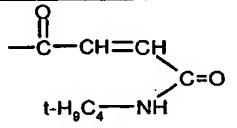
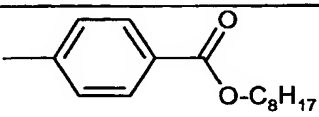
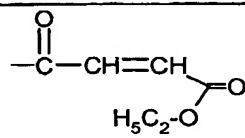
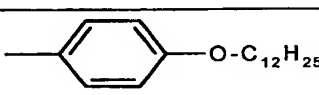
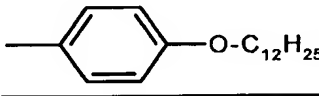
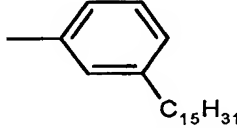
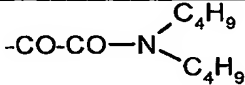
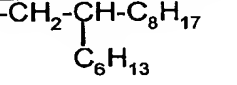
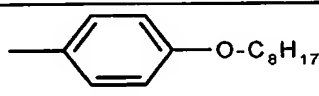
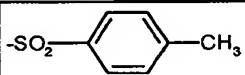
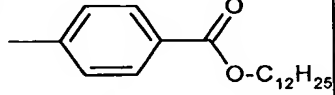
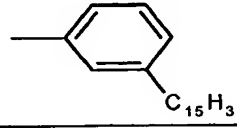
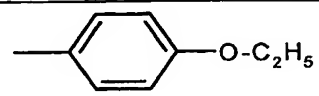
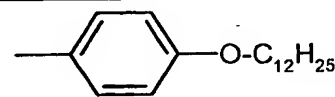
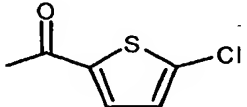
VII-3 with  $R^{11} = C_2H_5$ ,  $R^{12} = n-C_3H_7$ ,  $R^{13} = R^{14} = t-C_5H_{11}$ ,

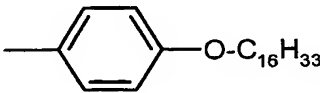
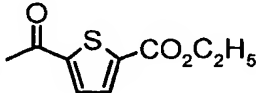
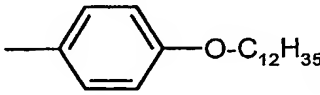
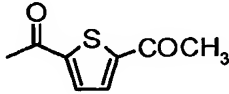
VII-4 with  $R^{11} = CH_3$ ,  $R^{12} = C_2H_5$ ,  $R^{13} = R^{14} = t-C_5H_{11}$ .

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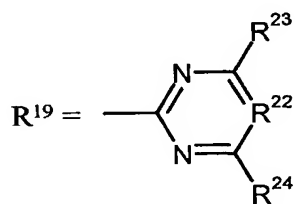
Examples of cyan couplers according to formula (VIII) with  $p = 2$  are:

No.	R <sup>16</sup>	R <sup>17</sup>	R <sup>15</sup>	R <sup>19</sup>	R <sup>18</sup>
VIII-1	-C <sub>2</sub> H <sub>5</sub>	H			-Cl
VIII-2	-C <sub>2</sub> H <sub>5</sub>	H			-H
VIII-3	-C <sub>6</sub> H <sub>13</sub>	H			-OCH <sub>2</sub> CH <sub>2</sub> - SCH <sub>2</sub> COOH
VIII-4	-Phenyl	H			-Cl
VIII-5	-CH <sub>3</sub>	-CH <sub>3</sub>	-C <sub>16</sub> H <sub>33</sub>		-Cl
VIII-6	-Phenyl	H	-C <sub>12</sub> H <sub>27</sub>		-SCH <sub>2</sub> CH <sub>2</sub> - COOH
VIII-7	-C <sub>2</sub> H <sub>5</sub>	H			-O-CH <sub>2</sub> - COOCH <sub>3</sub>
VIII-8	C <sub>12</sub> H <sub>25</sub>	H			-Cl
VIII-9	-C <sub>3</sub> H <sub>7</sub> -i	H			-Cl
VIII-10	-CH <sub>3</sub>	-CH <sub>3</sub>			
VIII-11	-C <sub>2</sub> H <sub>5</sub>	H			-Cl
VIII-12	-phenyl	H	-C <sub>16</sub> H <sub>33</sub>		H

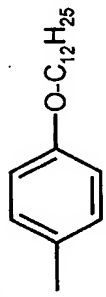
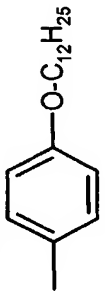
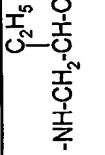
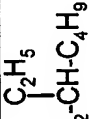
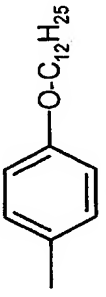
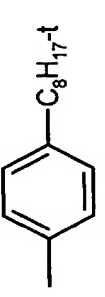
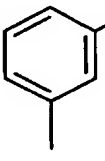
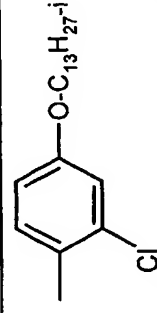
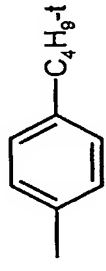
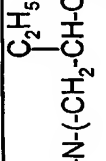
No.	R <sup>16</sup>	R <sup>17</sup>	R <sup>15</sup>	R <sup>19</sup>	R <sup>18</sup>
VIII-13	-C <sub>12</sub> H <sub>25</sub>	H			-Cl
VIII-14	-C <sub>4</sub> H <sub>9</sub>	H			-OCH <sub>2</sub> COOCH <sub>3</sub>
VIII-15	-CH <sub>3</sub>	-CH <sub>3</sub>			-Cl
VIII-16	-C <sub>2</sub> H <sub>5</sub>	H		-SO <sub>2</sub> -C <sub>4</sub> H <sub>9</sub>	-Cl
VIII-17	-C <sub>2</sub> H <sub>5</sub>	H		-CO-O-C <sub>4</sub> H <sub>9</sub> -i	-Cl
VIII-18	-C <sub>3</sub> H <sub>7</sub> -i	H			-OCH <sub>2</sub> - COOCH <sub>3</sub>
VIII-19	-phenyl	H		-SO <sub>2</sub> -NH-C <sub>4</sub> H <sub>9</sub> -t	H
VIII-20	-C <sub>6</sub> H <sub>13</sub>	H			H
VIII-21	-CH <sub>3</sub>	-CH <sub>3</sub>		-CO-CO-OC <sub>2</sub> H <sub>5</sub>	-Cl
VIII-22	-C <sub>4</sub> H <sub>9</sub>	H		-SO <sub>2</sub> -CH <sub>3</sub>	-Cl
VIII-23	-phenyl	-phenyl	-C <sub>12</sub> H <sub>25</sub>	-SO <sub>2</sub> -C <sub>4</sub> H <sub>9</sub>	-SCH <sub>2</sub> CH <sub>2</sub> - COOH
VIII-24	-C <sub>12</sub> H <sub>25</sub>	H		-CO-O-C <sub>2</sub> H <sub>5</sub>	-Cl
VIII-25	-C <sub>2</sub> H <sub>5</sub>	H			-Cl

No.	R <sup>16</sup>	R <sup>17</sup>	R <sup>15</sup>	R <sup>19</sup>	R <sup>18</sup>
VIII-26	-CH <sub>3</sub>	H			-Cl
VIII-27	-C <sub>2</sub> H <sub>5</sub>	H			-Cl

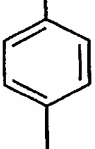
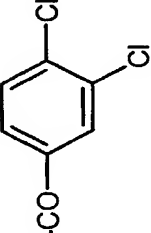
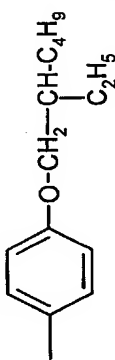
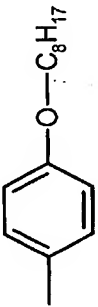
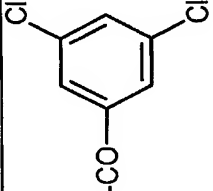
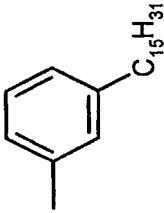
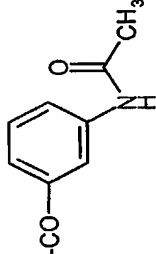
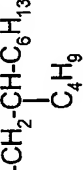
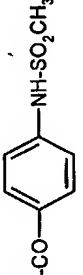
Examples of cyan couplers according to formula (VIII) with  $p = 2$   
and



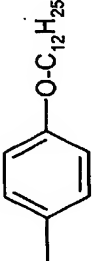
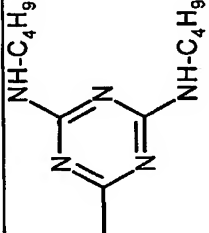
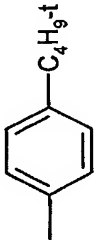
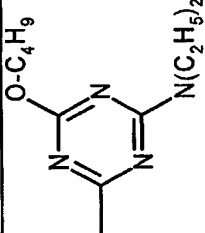
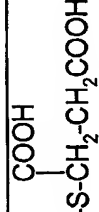
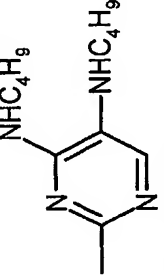
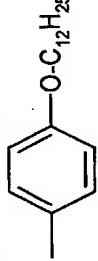
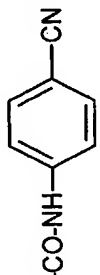
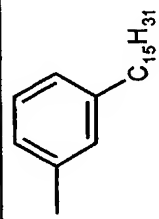
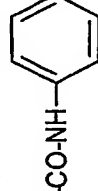
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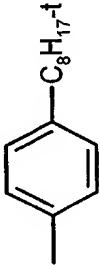
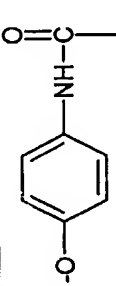
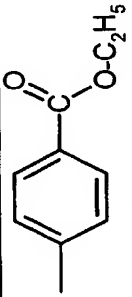
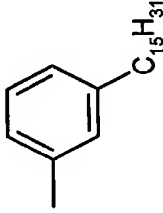
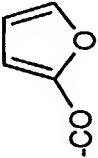
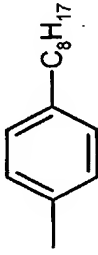
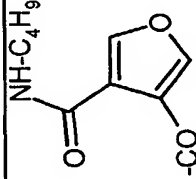
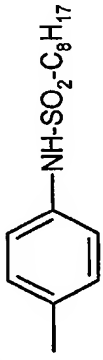
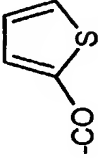
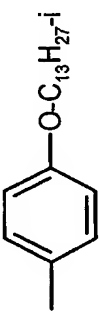
Nr.	R <sup>16</sup>	R <sup>17</sup>	R <sup>15</sup>	R <sup>23</sup>	R <sup>24</sup>	R <sup>22</sup>	R <sup>18</sup>
VIII-28	-C <sub>2</sub> H <sub>5</sub>	H		-N(C <sub>4</sub> H <sub>9</sub> ) <sub>2</sub>	-N(C <sub>4</sub> H <sub>9</sub> ) <sub>2</sub>	-N=	-C-
VIII-29	-C <sub>2</sub> H <sub>5</sub>	H		 -NH-CH <sub>2</sub> -CH(C <sub>2</sub> H <sub>5</sub> )-C <sub>4</sub> H <sub>9</sub>	 -NH-CH <sub>2</sub> -CH(C <sub>2</sub> H <sub>5</sub> )-C <sub>4</sub> H <sub>9</sub>	-N=	-Cl
VIII-30	-C <sub>2</sub> H <sub>5</sub>	H		-OCH <sub>3</sub>	-OCH <sub>3</sub>	-N=	-Cl
VIII-31	-C <sub>6</sub> H <sub>13</sub>	H		-Cl	-NH-C <sub>4</sub> H <sub>9</sub>	-C(NHC <sub>4</sub> H <sub>9</sub> )=	H
VIII-32	-phenyl	H	-C <sub>12</sub> H <sub>25</sub>	-OCH <sub>3</sub>	-N(C <sub>4</sub> H <sub>9</sub> ) <sub>2</sub>	-N=	-OCH <sub>2</sub> COOCH <sub>3</sub>
VIII-33	-CH <sub>3</sub>	-CH <sub>3</sub>		-NH-C <sub>4</sub> H <sub>9</sub>	-NH-C <sub>4</sub> H <sub>9</sub>	-	-Cl
VIII-34	H	H		-OCH <sub>3</sub>	-NH-C <sub>4</sub> H <sub>9</sub>	-N=	-S-CH <sub>2</sub> CH <sub>2</sub> -COOH
VIII-35	-CH <sub>3</sub>	H		-Cl	 -N(-CH <sub>2</sub> -CH(C <sub>2</sub> H <sub>5</sub> )-C <sub>4</sub> H <sub>9</sub> ) <sub>2</sub>	-N=	-Cl

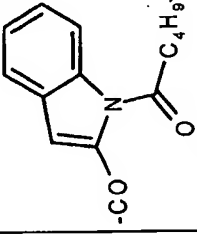
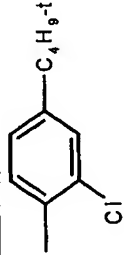
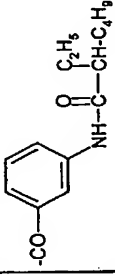
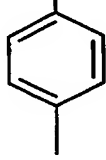
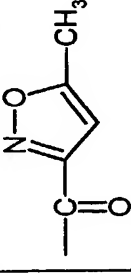
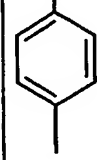
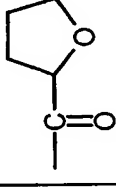
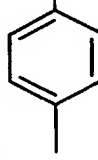
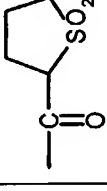

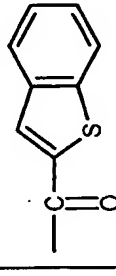
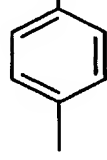
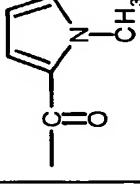
Examples of cyan couplers according to formula (VIII) with  $p = 1$  are:

Nr.	R <sup>16</sup>	R <sup>17</sup>	R <sup>15</sup>	R <sup>19</sup>	R <sup>18</sup>
VIII-36	-C <sub>2</sub> H <sub>5</sub>	H			-Cl
VIII-37	-C <sub>4</sub> H <sub>9</sub>	H		-CO-C <sub>3</sub> F <sub>7</sub>	-Cl
VIII-38	-C <sub>6</sub> H <sub>13</sub>	H			-OCH <sub>2</sub> CH <sub>2</sub> -S-CH <sub>2</sub> COOH
VIII-39	-CH <sub>3</sub>	-CH <sub>3</sub>			H
VIII-40	-Phenyl	H			-Cl

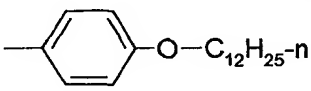
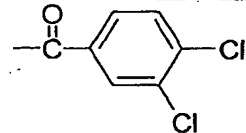
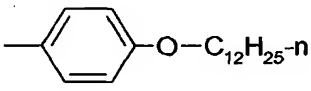
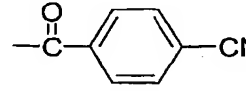
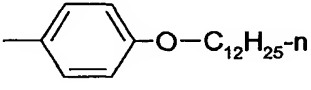
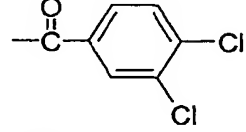
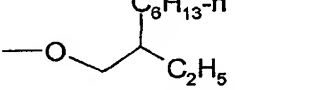
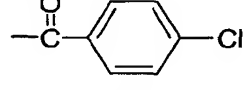
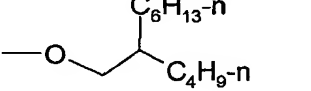
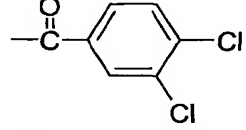


Nr.	R <sup>16</sup>	R <sup>17</sup>	R <sup>15</sup>	R <sup>19</sup>	R <sup>18</sup>
VIII-41	-C <sub>2</sub> H <sub>5</sub>	H			H
VIII-42	-C <sub>12</sub> H <sub>25</sub>	H			
VIII-43	-C <sub>4</sub> H <sub>9</sub>	H	-C <sub>12</sub> H <sub>25</sub>		-Cl
VIII-44	-C <sub>2</sub> H <sub>5</sub>	H		-SO <sub>2</sub> -C <sub>4</sub> H <sub>9</sub>	-Cl
VIII-45	-C <sub>3</sub> H <sub>7</sub> -i	H	-C <sub>16</sub> H <sub>33</sub>		-O-CH <sub>2</sub> -COO-CH <sub>3</sub>
VIII-46	-CH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> -				-Cl

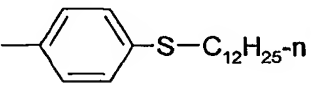
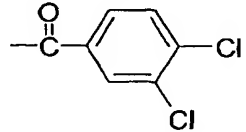
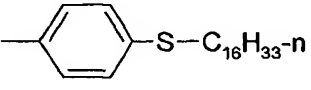
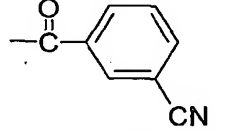
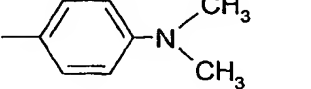
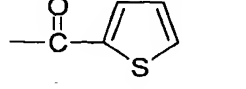
Nr.	R <sup>16</sup>	R <sup>17</sup>	R <sup>15</sup>	R <sup>19</sup>	R <sup>18</sup>
VIII-47	-C <sub>2</sub> H <sub>5</sub>	-C <sub>2</sub> H <sub>5</sub>		-CO-O-C <sub>4</sub> H <sub>9</sub> -i	H
VIII-48	-phenyl	H	-C <sub>12</sub> H <sub>25</sub>	-CO-CO-N(C <sub>4</sub> H <sub>9</sub> ) <sub>2</sub>	 HOOC-CH <sub>2</sub> -CH <sub>2</sub>
VIII-49	-C <sub>12</sub> H <sub>25</sub>	H		-CO-CH=CH-CO-N(C <sub>2</sub> H <sub>5</sub> ) <sub>2</sub>	-Cl
VIII-50	-C <sub>2</sub> H <sub>5</sub>	H			-Cl
VIII-51	-C <sub>6</sub> H <sub>13</sub>	H			H
VIII-52	-C <sub>4</sub> H <sub>9</sub>	H			-Cl
VIII-53	-CH <sub>3</sub>	H		-CO-CH=CH-CO-CH <sub>3</sub>	-Cl

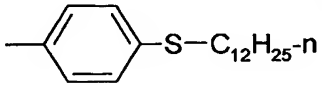
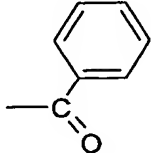
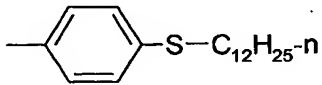
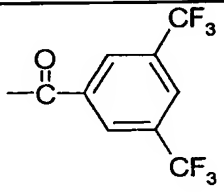
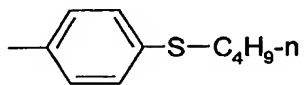
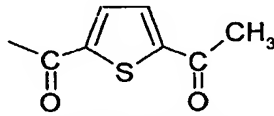
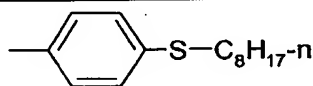
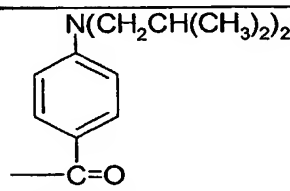
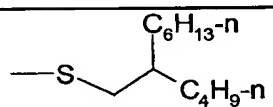
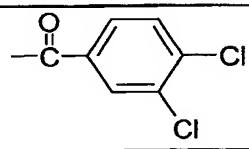
Nr.	R <sup>16</sup>	R <sup>17</sup>	R <sup>15</sup>	R <sup>19</sup>	R <sup>18</sup>
VIII-54	-Phenyl	H	$-\text{CH}_2-\text{CH}-\text{C}_4\text{H}_9$   $\text{C}_2\text{H}_5$		H
VIII-55	-C <sub>2</sub> H <sub>5</sub>	H			-Cl
VIII-56	-C <sub>2</sub> H <sub>5</sub>	H			Cl
VIII-57	-C <sub>3</sub> H <sub>7</sub>	H			Cl
VIII-58	-C <sub>2</sub> H <sub>5</sub>	H			H
VIII-59	-H	H			Cl
VIII-60	-C <sub>2</sub> H <sub>5</sub>	H			Cl

Examples of group (6) cyan couplers according to formula (VIII) with  $p = 2$  are:

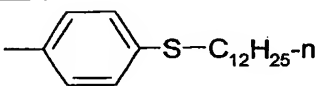
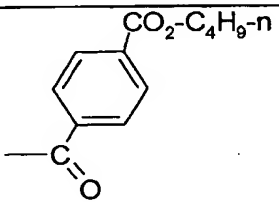
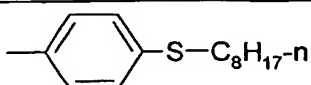
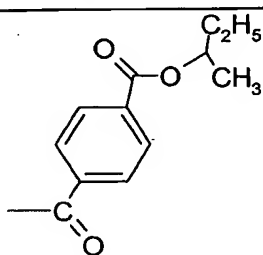
No.	R <sup>16</sup>	R <sup>17</sup>	R <sup>15</sup>	R <sup>19</sup>	R <sup>18</sup>
VIII-61	-C <sub>2</sub> H <sub>5</sub>	H			-Cl
VIII-62	-CH <sub>3</sub>	H			-Cl
VIII-63	-C <sub>2</sub> H <sub>5</sub>	H			-O-CH <sub>2</sub> -CO- NH-CH <sub>2</sub> -CH <sub>2</sub> - O-CH <sub>3</sub>
VIII-64	-C <sub>2</sub> H <sub>5</sub>	H			-Cl
VIII-65	-C <sub>2</sub> H <sub>5</sub>	H			-Cl

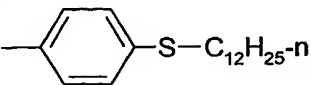
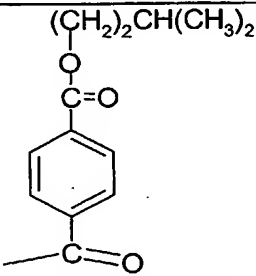
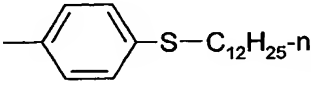
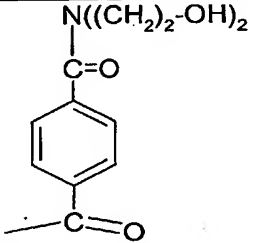
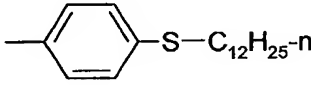
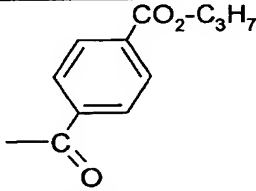
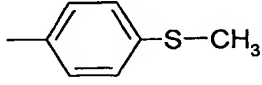
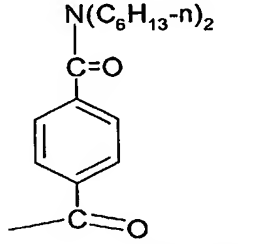
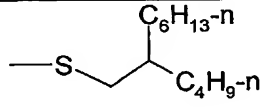
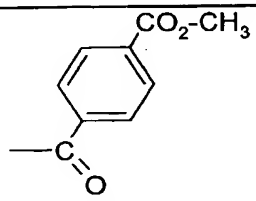
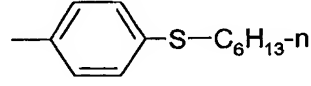
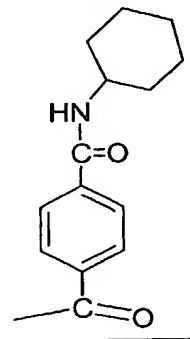
Examples of group (7) cyan couplers according to formula (VIII) with  $p = 2$  are:

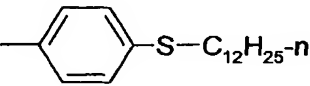
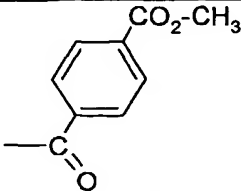
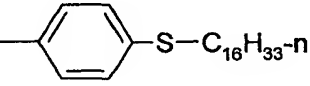
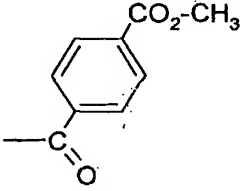
No.	R <sup>16</sup>	R <sup>17</sup>	R <sup>15</sup>	R <sup>19</sup>	R <sup>18</sup>
VIII-66	-C <sub>2</sub> H <sub>5</sub>	H			-Cl
VIII-67	-C <sub>2</sub> H <sub>5</sub>	H			-O-CH <sub>2</sub> -CH <sub>2</sub> - CO-NH-CH <sub>3</sub>
VIII-68	-C <sub>12</sub> H <sub>25</sub> - n	H			Cl

No.	R <sup>16</sup>	R <sup>17</sup>	R <sup>15</sup>	R <sup>19</sup>	R <sup>18</sup>
VIII-69	-C <sub>2</sub> H <sub>5</sub>	H			-Cl
VIII-70	-C <sub>2</sub> H <sub>5</sub>	H			Cl
VIII-71	-C <sub>2</sub> H <sub>5</sub>	H			Cl
VIII-72	-C <sub>2</sub> H <sub>5</sub>	H			Cl
VIII-73	-C <sub>2</sub> H <sub>5</sub>	H			Cl

Examples of group (8) cyan couplers according to formula (VIII) with  $p = 2$  are:

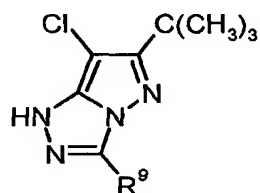
No.	R <sup>16</sup>	R <sup>17</sup>	R <sup>15</sup>	R <sup>19</sup>	R <sup>18</sup>
VIII-74	-C <sub>2</sub> H <sub>5</sub>	H			-Cl
VIII-75	-C <sub>2</sub> H <sub>5</sub>	H			-Cl

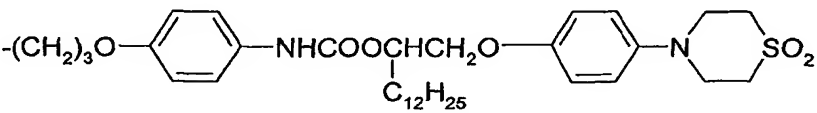
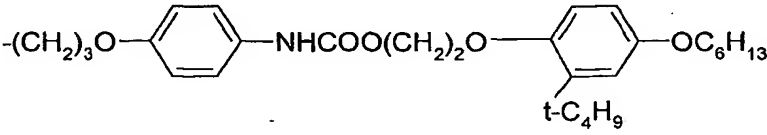
No.	R <sup>16</sup>	R <sup>17</sup>	R <sup>15</sup>	R <sup>19</sup>	R <sup>18</sup>
VIII-76	-CH <sub>3</sub>	H			Cl
VIII-77	-C <sub>2</sub> H <sub>5</sub>	H			-Cl
VIII-78	-C <sub>2</sub> H <sub>5</sub>	H			-O-CH <sub>2</sub> -CO- NH-CH <sub>2</sub> -CH <sub>2</sub> - O-CH <sub>3</sub>
VIII-79	-C <sub>2</sub> H <sub>5</sub>	H			Cl
VIII-80	-CH <sub>3</sub>	H			Cl
VIII-81	-C <sub>2</sub> H <sub>5</sub>	H			Cl

No.	R <sup>16</sup>	R <sup>17</sup>	R <sup>15</sup>	R <sup>19</sup>	R <sup>18</sup>
VIII-82	-C <sub>2</sub> H <sub>5</sub>	H			-O-CH <sub>2</sub> -CO- NH-CH <sub>2</sub> -CH <sub>2</sub> - O-CH <sub>3</sub>
VIII-83	-C <sub>2</sub> H <sub>5</sub>	H			-O-CH <sub>2</sub> -CH <sub>2</sub> - CO-NH-CH <sub>3</sub>

The preparation of cyan couplers according to formula (VIII) proceeds analogously to the syntheses disclosed in US 5,686,235 herein incorporated by reference.

Examples of magenta couplers according to formula (V) are:



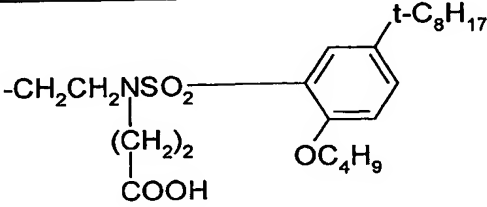
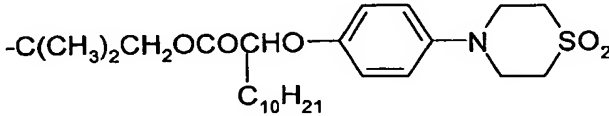
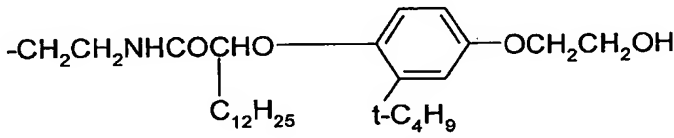
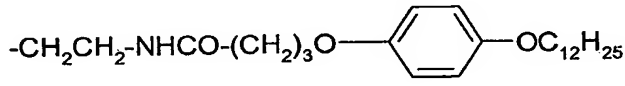
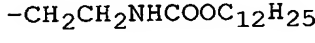
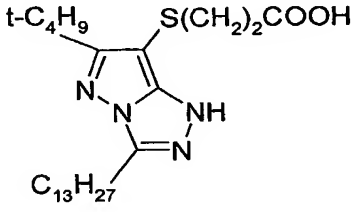
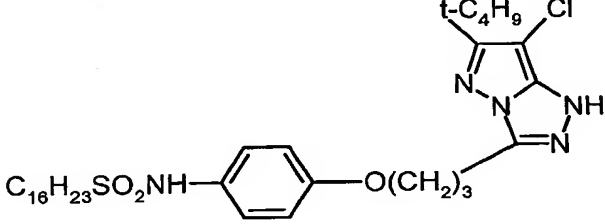
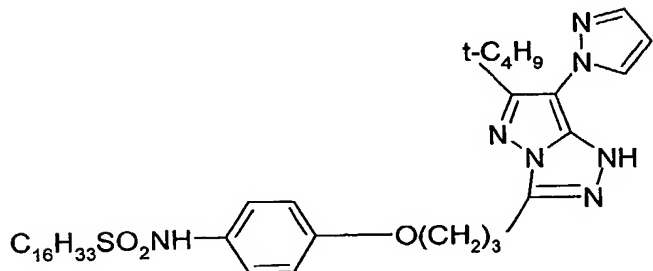
Coupler	R <sup>9</sup>
V-1	-C <sub>13</sub> H <sub>27</sub>
V -2	-(CH <sub>2</sub> ) <sub>3</sub> SO <sub>2</sub> C <sub>12</sub> H <sub>25</sub>
V -3	
V -4	

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Coupler	R <sup>9</sup>
V -5	$-(\text{CH}_2)_3\text{O}-\text{C}_6\text{H}_4-\text{NHSO}_2-\text{C}_6\text{H}_3(\text{OC}_4\text{H}_9)(\text{t-C}_8\text{H}_{17})$
V -6	$-(\text{CH}_2)_3\text{O}-\text{C}_6\text{H}_4-\text{NHSO}_2-\text{C}_6\text{H}_3(\text{O}(\text{CH}_2)_3\text{COOH})(\text{t-C}_8\text{H}_{17})$
V -7	$-(\text{CH}_2)_2\text{NHCOC}_{13}\text{H}_{27}$
V -8	$-(\text{CH}_2)_2\text{NHCOC}(\text{C}_{10}\text{H}_{21})\text{HO}-\text{C}_6\text{H}_4-\text{N}(\text{SO}_2)\text{C}_6\text{H}_4$
V -9	$-(\text{CH}_2)_3\text{O}-\text{C}_6\text{H}_4-\text{NHCOC}(\text{C}_{12}\text{H}_{25})\text{H}-\text{CH}_2-\text{C}_6\text{H}_4-\text{N}(\text{SO}_2)\text{C}_6\text{H}_4$
V -10	$-(\text{CH}_2)_3\text{O}-\text{C}_6\text{H}_4-\text{NHCOC}(\text{C}_{12}\text{H}_{25})\text{H}-\text{CH}_2-\text{C}_6\text{H}_3(\text{OCH}_2\text{CH}_2\text{OH})(\text{t-C}_4\text{H}_9)$
V -11	$-\text{CH}_2\text{CH}_2\text{NHSO}_2-\text{C}_6\text{H}_3(\text{t-C}_8\text{H}_{17})(\text{OCH}_2\text{COOH})$
V -12	$-\text{CH}_2\text{CH}_2\text{NHSO}_2\text{C}_{16}\text{H}_{33}$
V -13	$-\text{CH}_2\text{CH}_2\text{NHCONHC}_{12}\text{H}_{25}$
V -14	$-(\text{CH}_2)_3\text{NHSO}_2\text{C}_{12}\text{H}_{25}$
V -15	$-\text{CH}_2\text{CH}_2\text{NHSO}_2-\text{C}_6\text{H}_3(\text{t-C}_8\text{H}_{17})(\text{OC}_4\text{H}_9)$
V -16	$-\text{CH}(\text{CH}_3)\text{CH}_2\text{CH}_2\text{NHSO}_2-\text{C}_6\text{H}_3(\text{t-C}_8\text{H}_{17})(\text{O-CH}_2\text{COOH})$

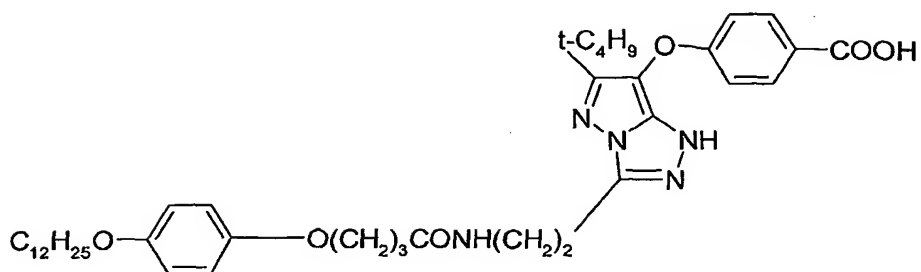


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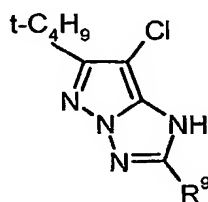
Coupler	R <sup>9</sup>
V -17	
V -18	
V -19	
V -20	
V -21	
and V -22	
V -23	
V -24	

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V -25



Examples of magenta couplers according to formula (VI) are:



Coupler	R <sup>9</sup>
VI-1	
VI -2	
VI -3	
VI -4	
VI -5	
VI -6	

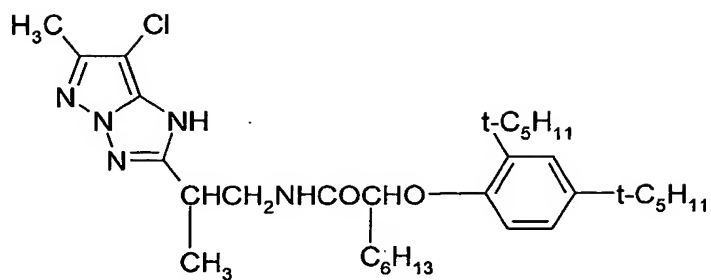
39

Coupler	R <sup>9</sup>
VI -7	$-\text{CH}_2\text{CH}_2\text{NHCOO}-\underset{\text{C}_{12}\text{H}_{25}}{\text{CH}}\text{CH}_2-\text{O}-\text{C}_6\text{H}_4-\text{N}(\text{CH}_2)_4\text{SO}_2$
VI -8	$-\text{CH}_2\text{CH}_2\text{NHCOCHO}-\underset{\text{C}_2\text{H}_5}{\text{C}}(\text{t-C}_5\text{H}_{11})_2-\text{C}_6\text{H}_4-\text{t-C}_5\text{H}_{11}$
VI -9	$-\text{CH}_2\text{CH}_2\text{NHCOC}_{13}\text{H}_{27}$
VI -10	$-\text{CH}_2\text{CH}_2\text{NHCOCHO}-\underset{\text{C}_4\text{H}_9}{\text{C}}(\text{t-C}_5\text{H}_{11})_2-\text{C}_6\text{H}_4-\text{t-C}_5\text{H}_{11}$
VI -11	$-(\text{CH}_2)_3\text{SO}_2\text{C}_{12}\text{H}_{25}$
VI -12	$-\text{CH}_2\text{CH}_2\text{NHSO}_2-\text{C}_6\text{H}_3(\text{OC}_4\text{H}_9)(\text{t-C}_8\text{H}_{17})$
VI -13	$-\underset{\text{CH}_3}{\text{CH}}-\text{CH}_2\text{SO}_2\text{C}_{12}\text{H}_{25}$
VI -14	$-\text{CH}_2\text{CH}_2\text{NHCOCHO}-\underset{\text{C}_2\text{H}_5}{\text{C}}(\text{t-C}_5\text{H}_{11})_2-\text{C}_6\text{H}_4-\text{t-C}_5\text{H}_{11}$
VI -15	$-\text{CH}_2\text{CH}_2\text{NHCOCHO}-\underset{\text{C}_{12}\text{H}_{25}}{\text{C}}(\text{t-C}_5\text{H}_{11})_2-\text{C}_6\text{H}_4-\text{N}(\text{CH}_2)_4\text{SO}_2$
VI -16	$-\text{C}_6\text{H}_4-\text{NHCOCHO}-\underset{\text{C}_6\text{H}_{13}}{\text{C}}(\text{OC}_{14}\text{H}_{29})(\text{t-C}_4\text{H}_9)-\text{C}_6\text{H}_4-$
VI -17	$-\text{C}_6\text{H}_4-\text{NHCOCHO}-\underset{\text{C}_6\text{H}_{13}}{\text{C}}(\text{OC}_6\text{H}_{13})(\text{t-C}_4\text{H}_9)-\text{C}_6\text{H}_4-$

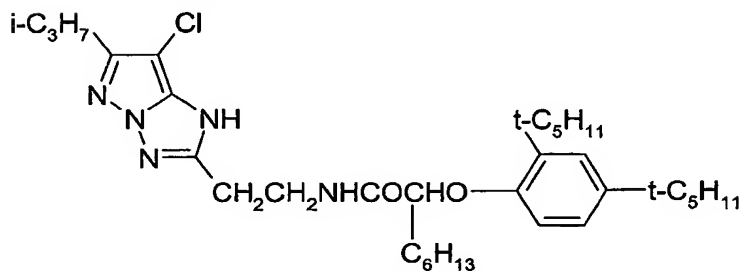
and

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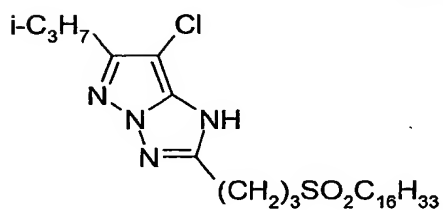
VI -18



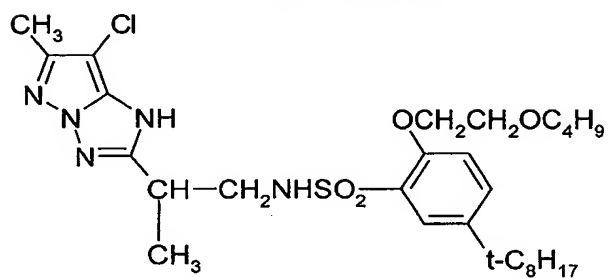
VI -19



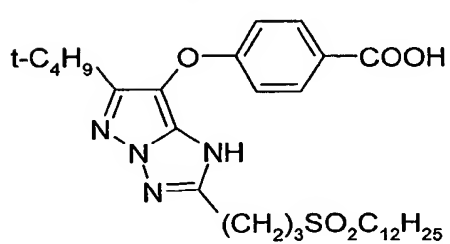
VI -20



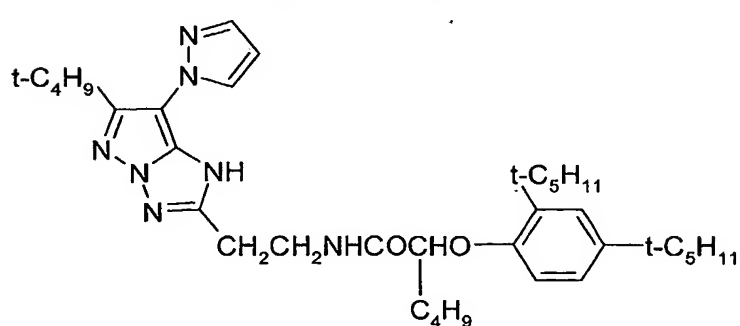
VI -21



VI -22

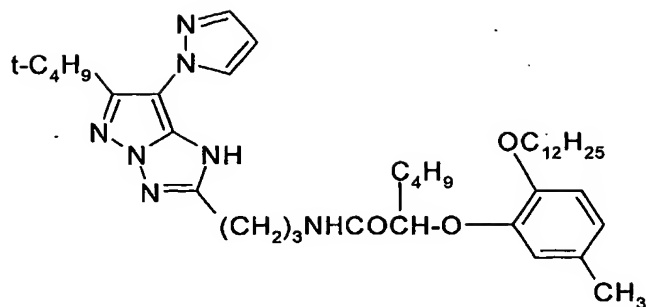


VI -23

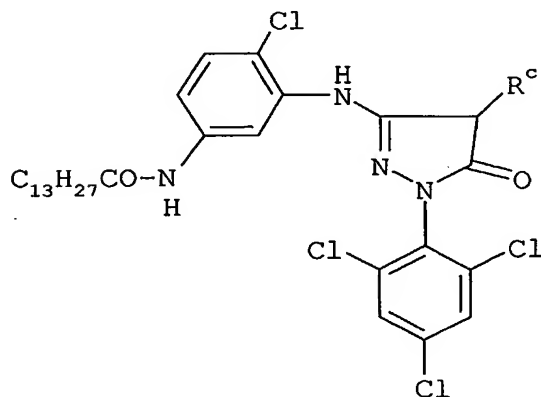


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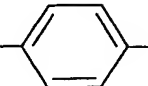
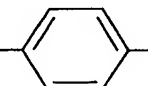
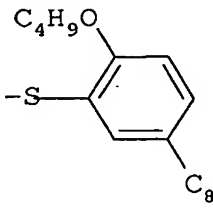
VI -24

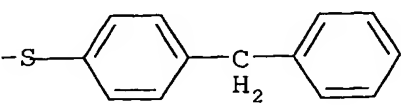
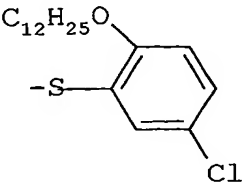
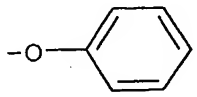
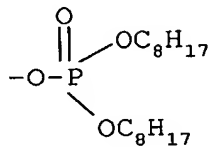
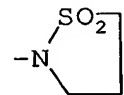
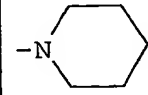
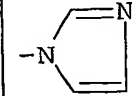
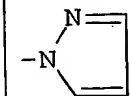


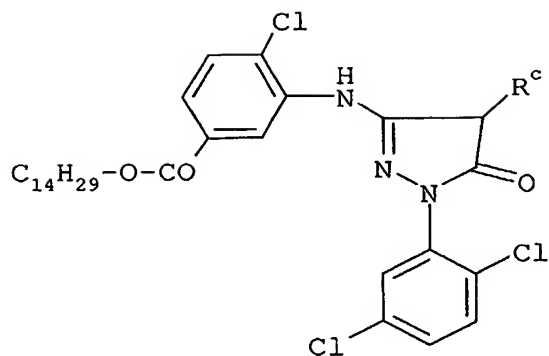
Examples of magenta couplers according to formula (XIV) are:



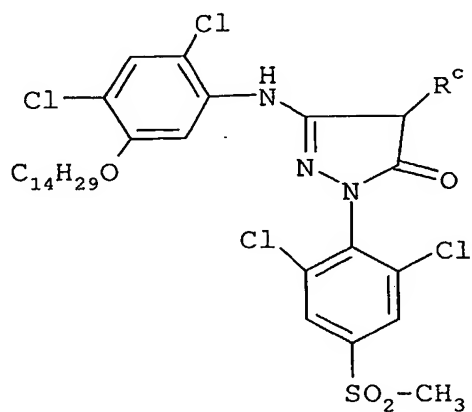
5

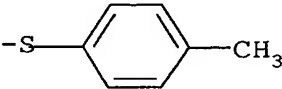
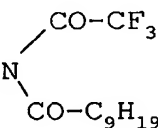
Coupler	R <sup>c</sup>
(XIV-1)	-H
(XIV-2)	-S-  -C <sub>4</sub> H <sub>9</sub> -t
(XIV-3)	-S-  -Cl
(XIV-4)	-S-  -C <sub>8</sub> H <sub>17</sub> -t

(XIV-5)	
(XIV-6)	
(XIV-7)	
(XIV-8)	
(XIV-9)	$\text{-NH-SO}_2\text{-C}_4\text{H}_9$
(XIV-10)	
(XIV-11)	
(XIV-12)	
(XIV-13)	

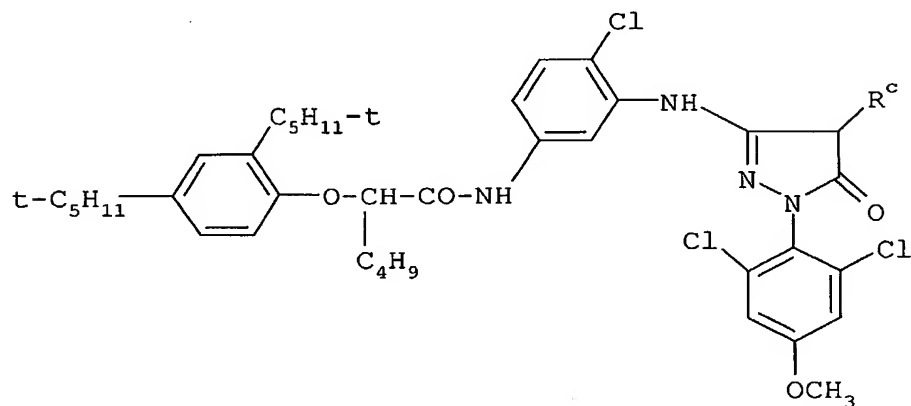


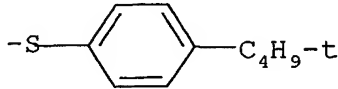
Coupler	R <sup>c</sup>
(XIV-14)	H
(XIV-15)	
(XIV-16)	
(XIV-17)	



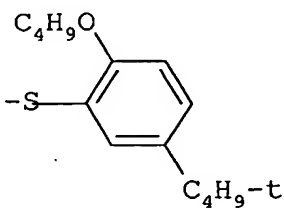
Coupler	R <sup>c</sup>
(XIV-18)	H
(XIV-19)	
(XIV-20)	

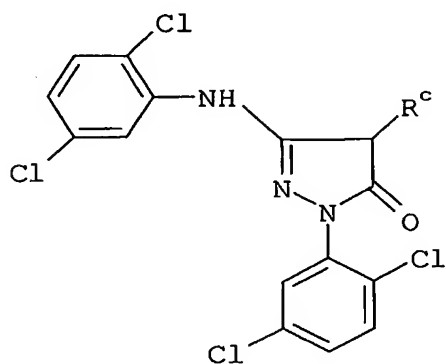
5



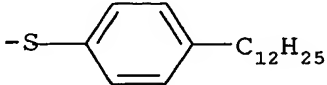
Coupler	R <sup>c</sup>
(XIV-21)	H
(XIV-22)	



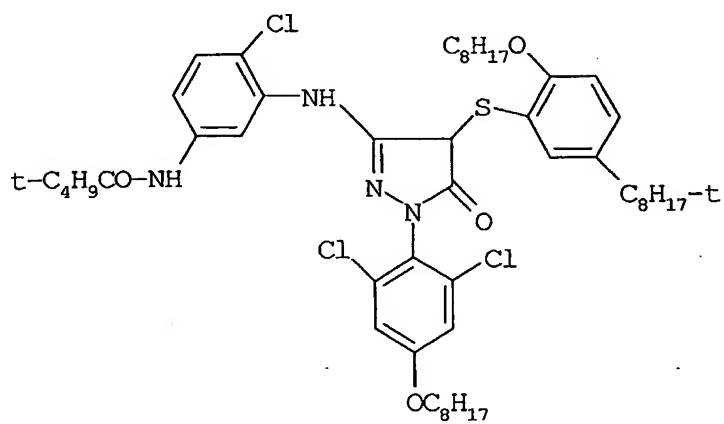
(XIV-23)	
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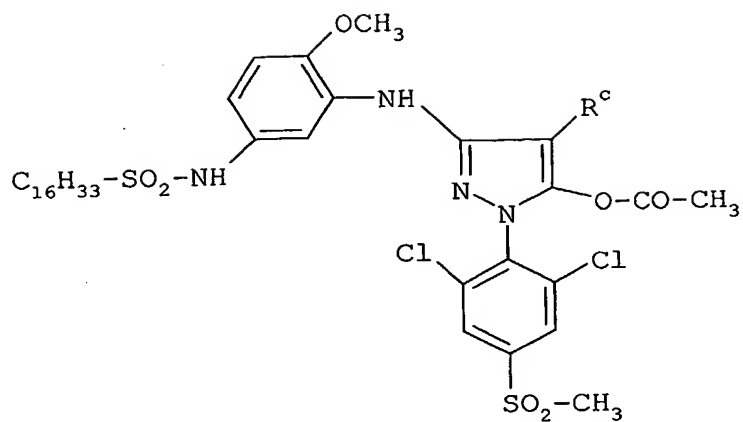


5

Coupler	R <sup>c</sup>
(XIV-24)	
(XIV-25)	-S-C <sub>12</sub> H <sub>25</sub>

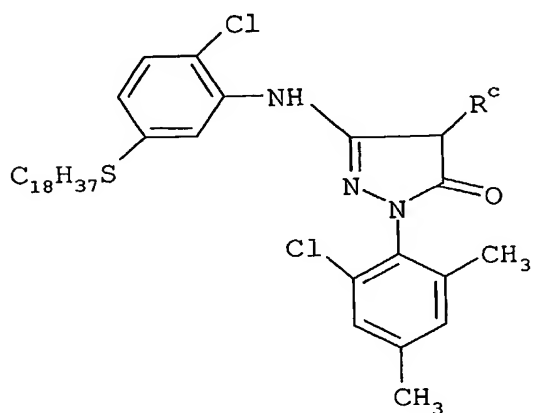
(XIV-26)



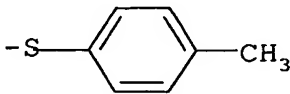


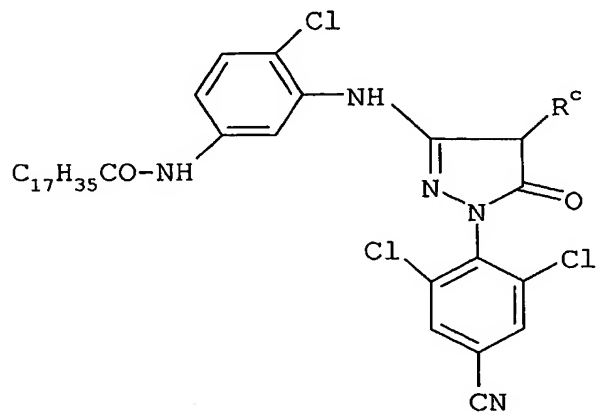
Coupler	R <sup>c</sup>
(XIV-27)	H
(XIV-28)	
(XIV-29)	

5

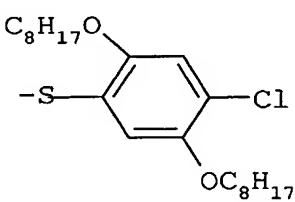
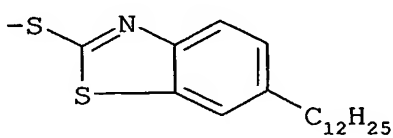


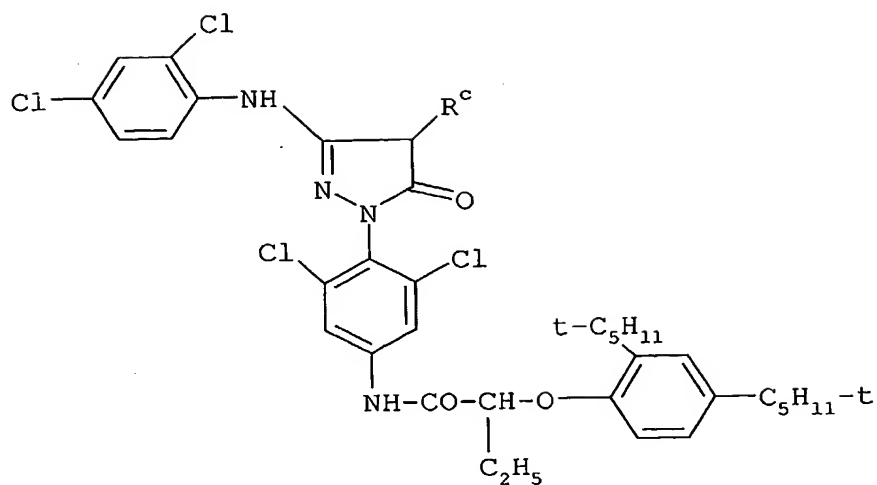
Coupler	R <sup>c</sup>

(XIV-30)	H
(XIV-31)	



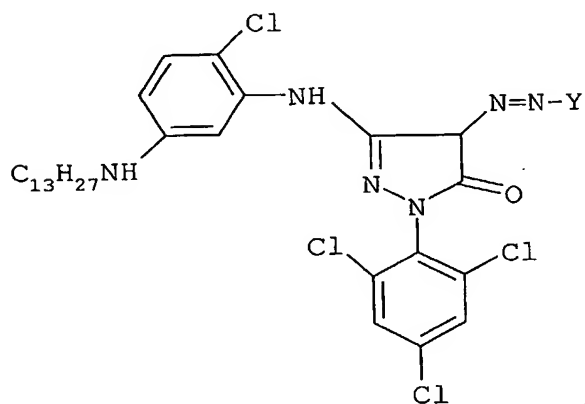
5

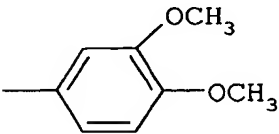
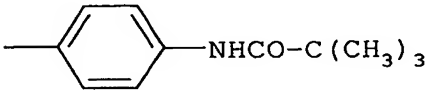
Coupler	R <sup>c</sup>
(XIV-32)	H
(XIV-33)	
(XIV-34)	



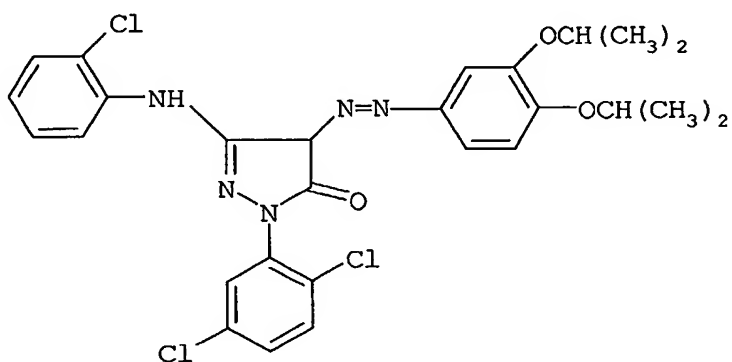
Coupler	R <sup>c</sup>
(XIV-35)	H
(XIV-36)	
(XIV-37)	

5

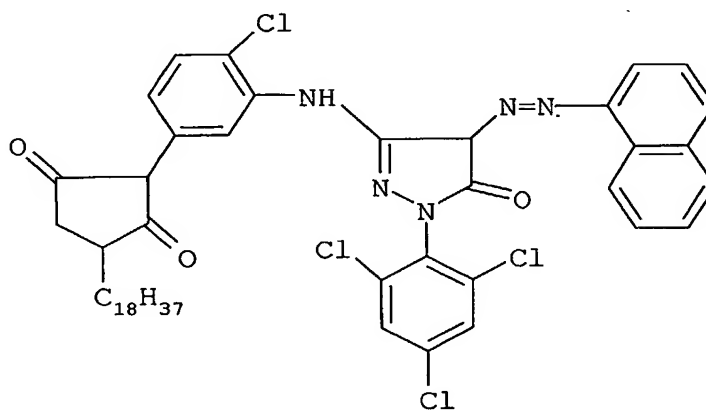


Coupler	Y
(XIV-38)	
(XIV-39)	

(XIV-40)

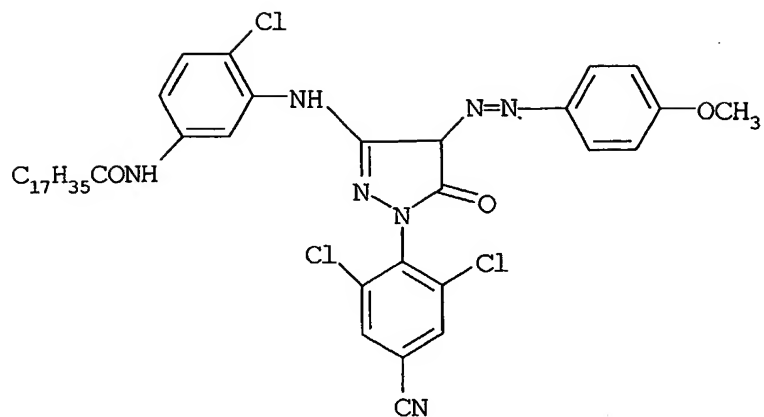


(XIV-41)

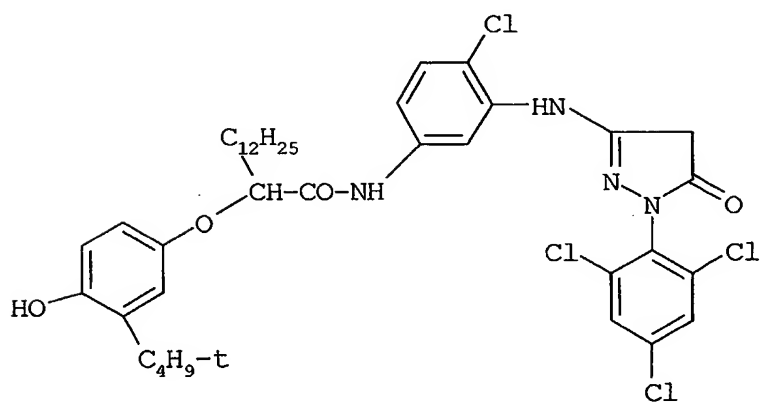


50

(XIV-42)

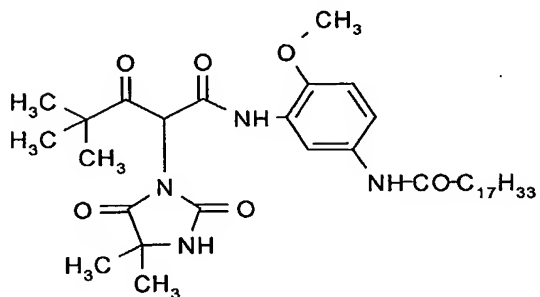


(XIV-43)



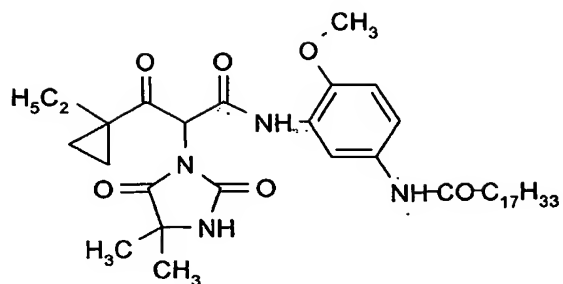
Examples of yellow couplers according to formula (IV) are:

IV-1

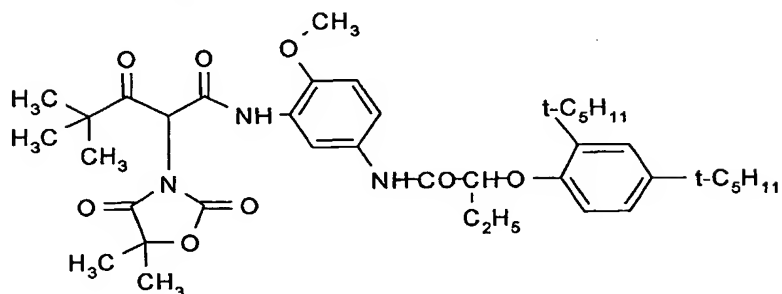


51

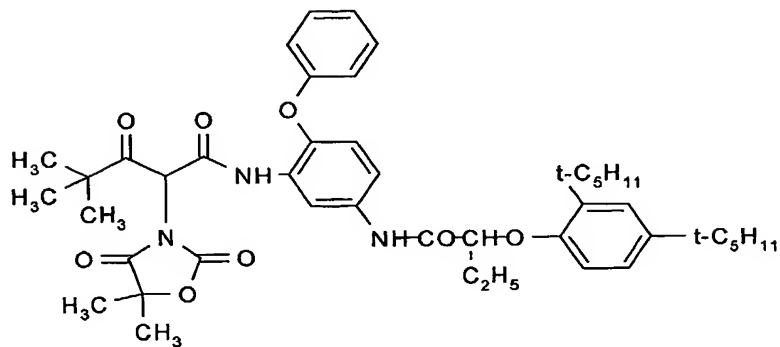
IV-2



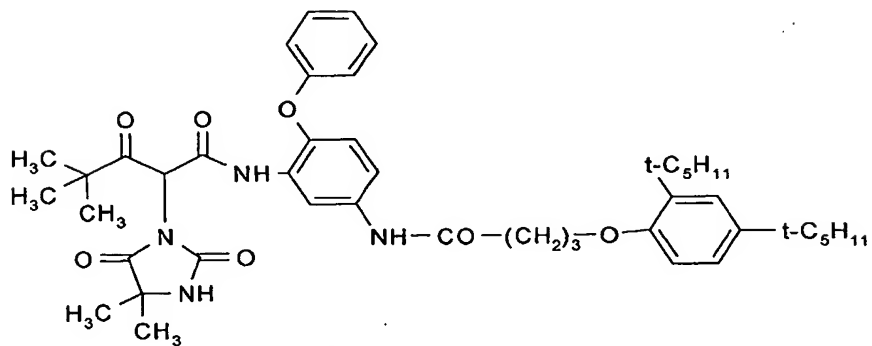
IV-3



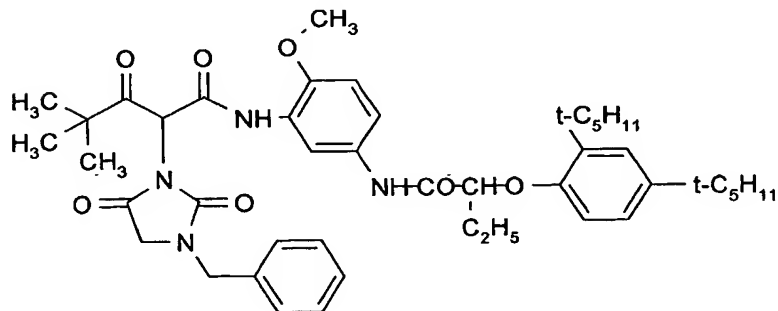
IV-4



IV-5

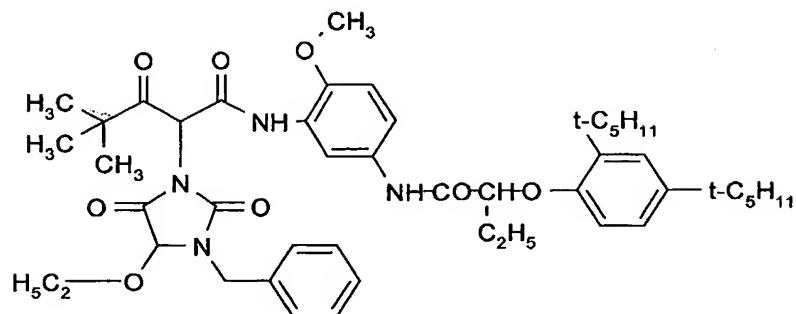


IV-6

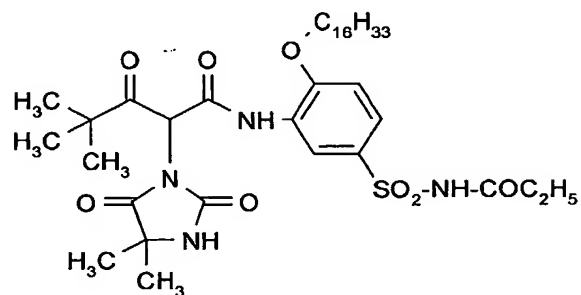


52

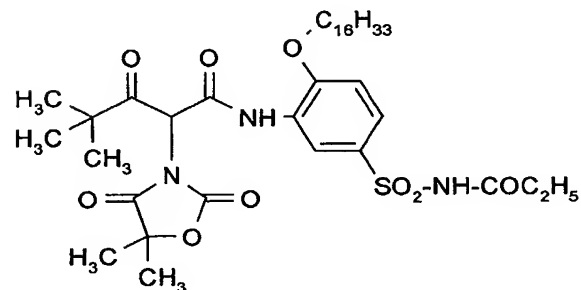
IV-7



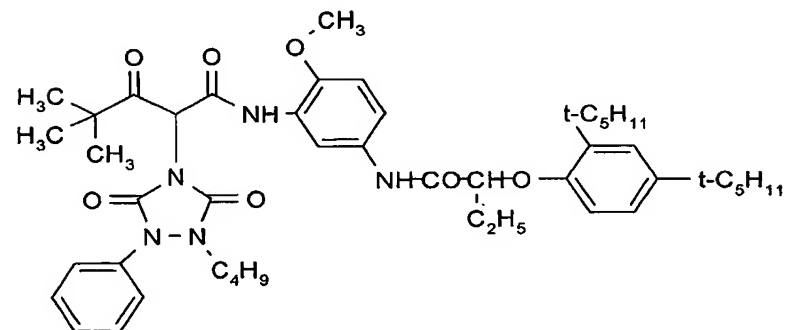
IV-8



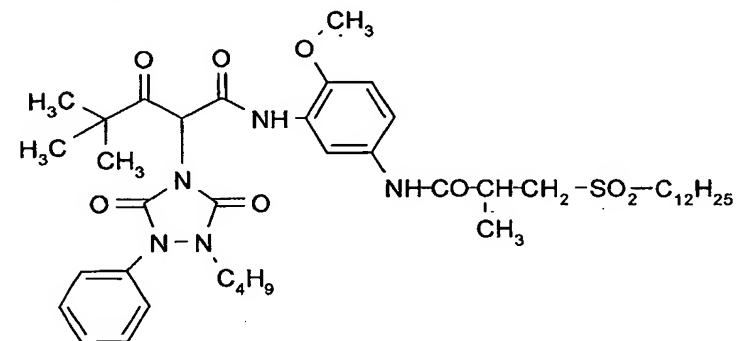
IV-9



IV-10



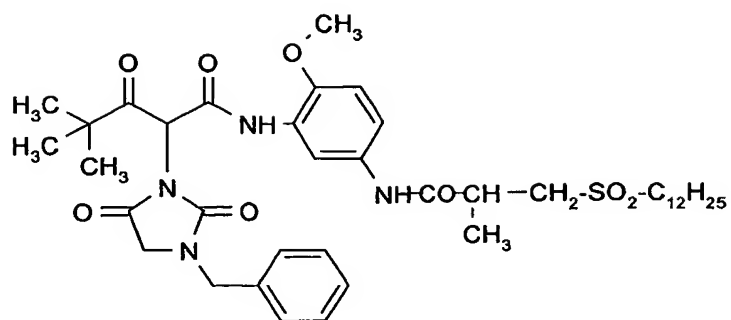
IV-11



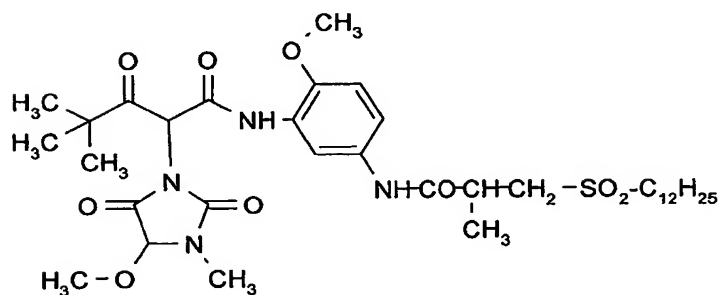


53

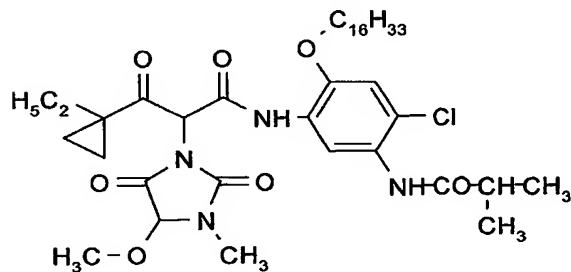
IV-12



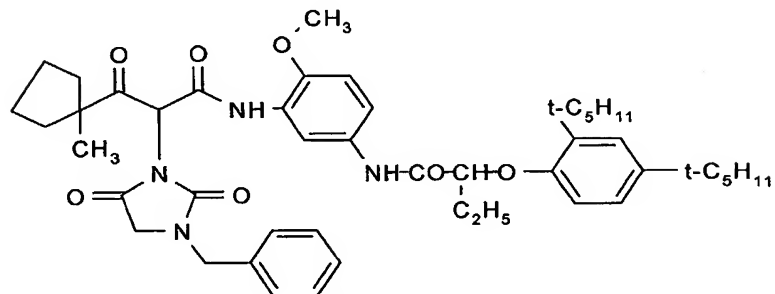
IV-13



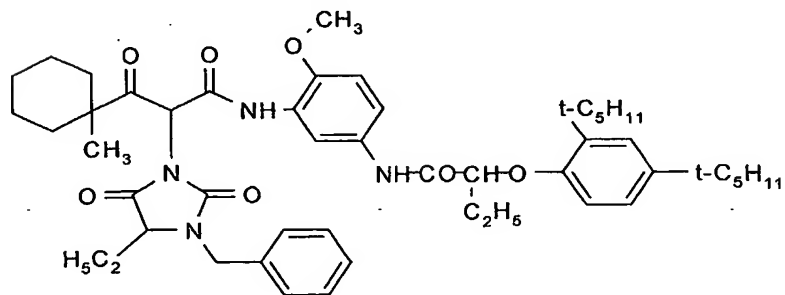
IV -14



IV-15

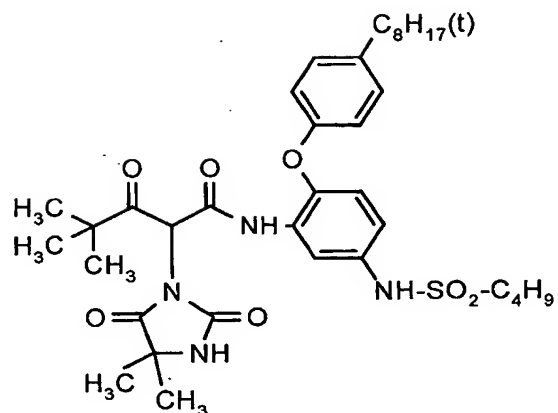


IV-16

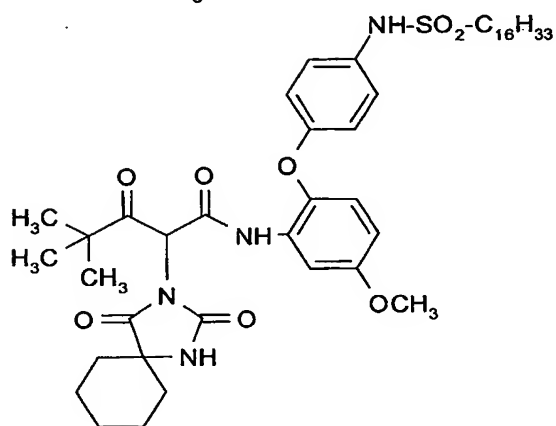


54

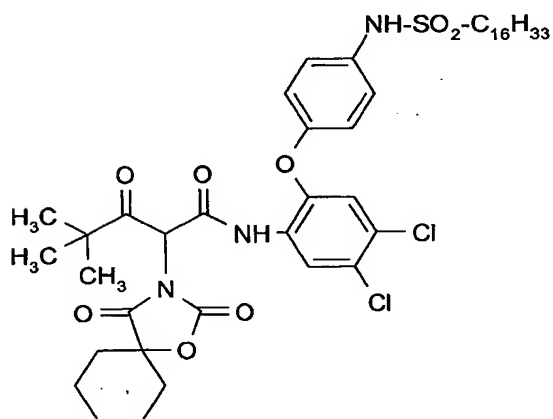
IV-17



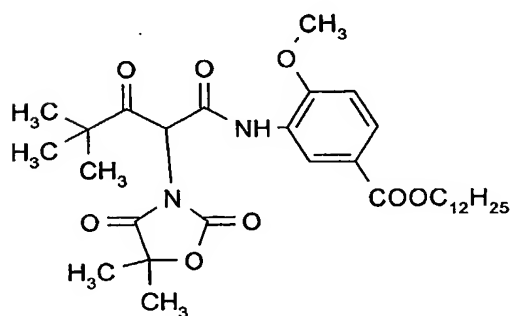
IV-18



IV-19

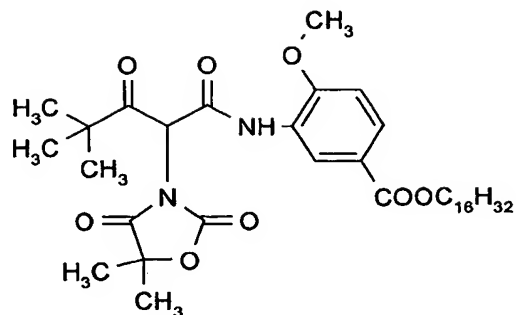


IV-20

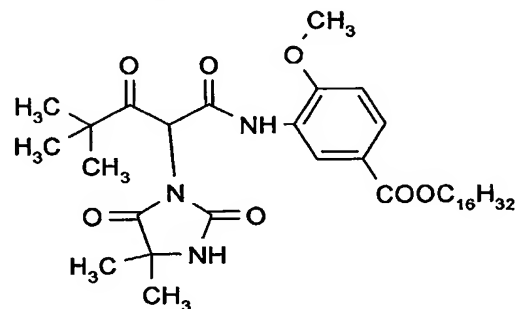


55

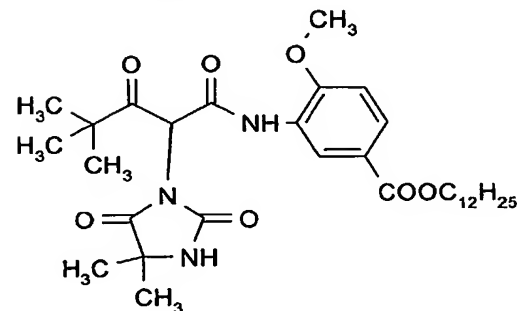
IV-21



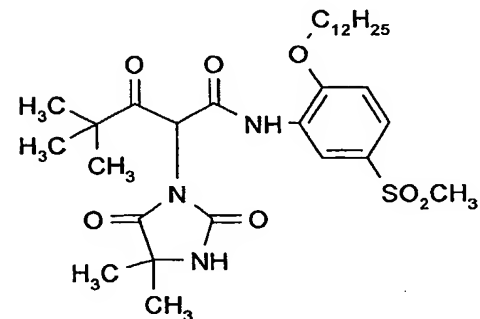
IV-22



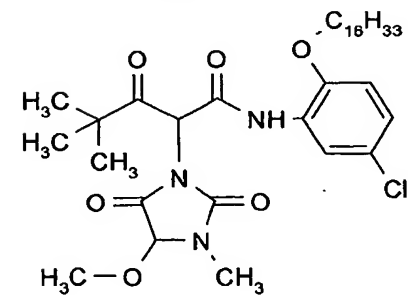
IV-23



IV-24

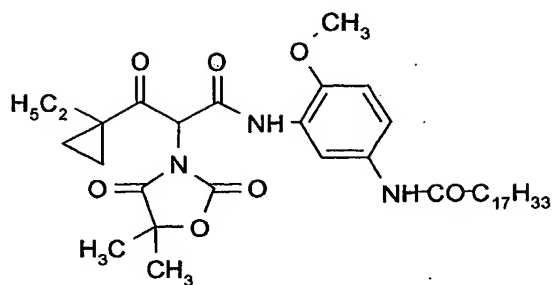


IV-25

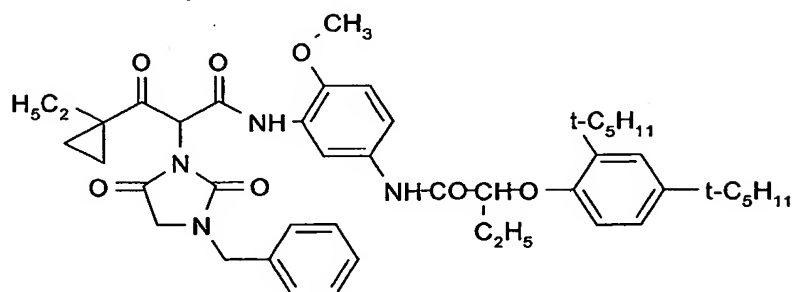


56

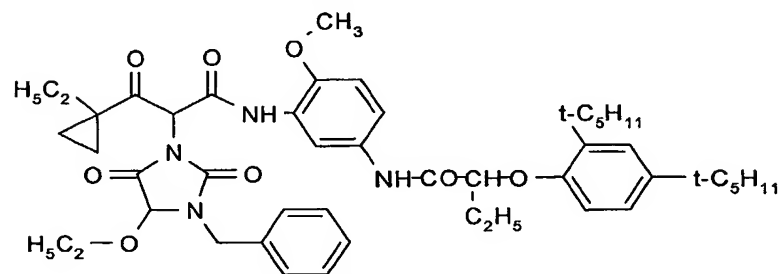
IV-26



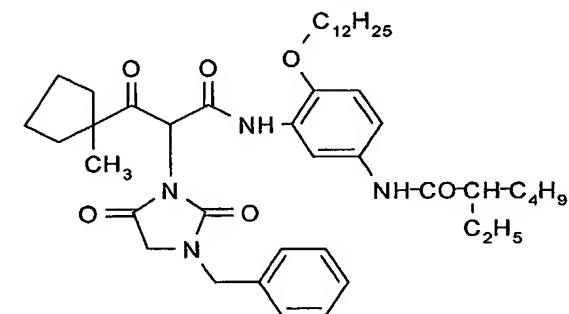
IV-27



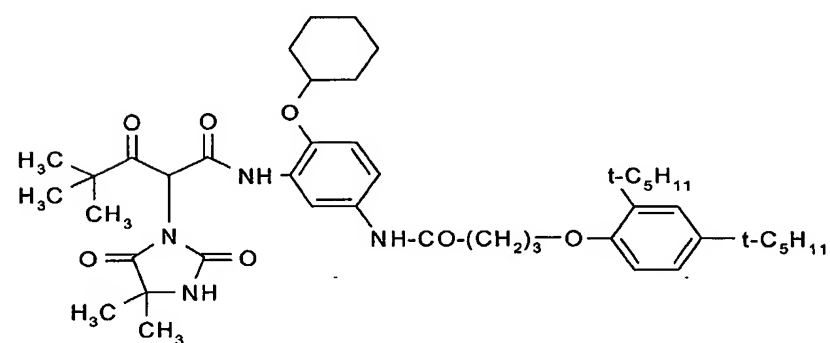
IV-28



IV-29

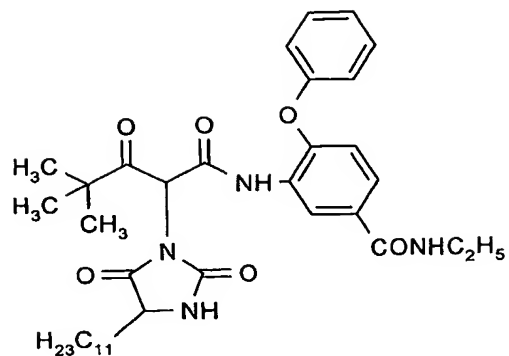


IV-30

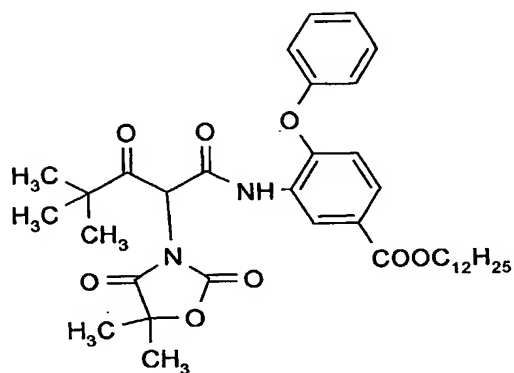


57

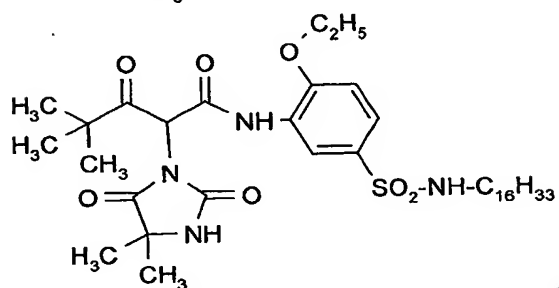
IV-31



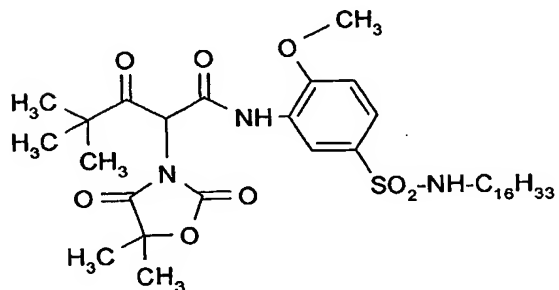
IV-32



IV-33

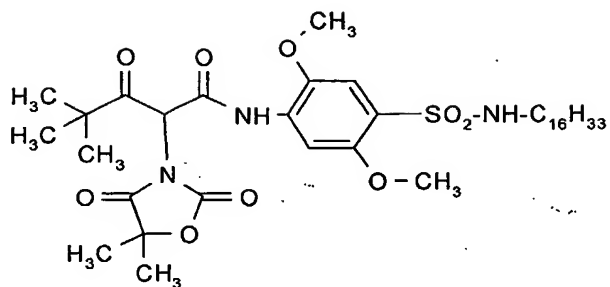


IV-34

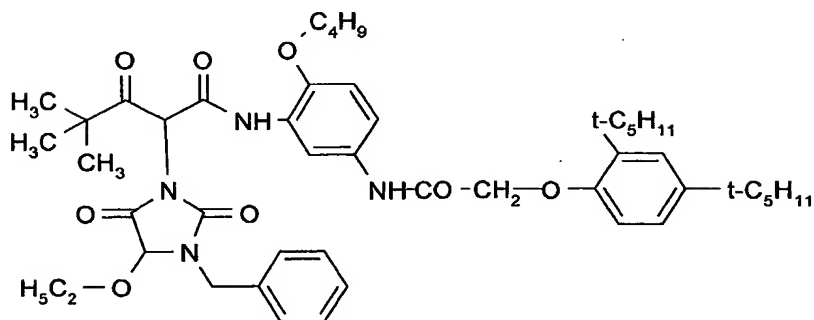


58

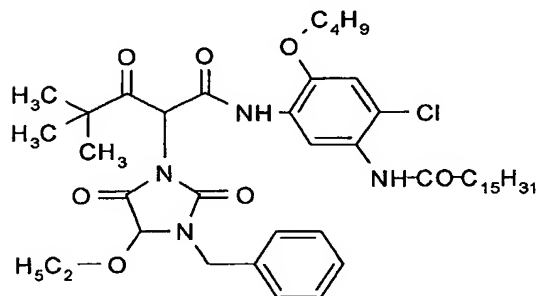
IV-35



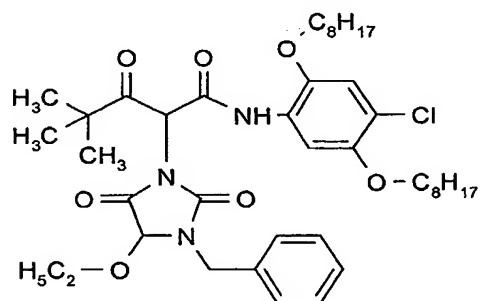
IV-36



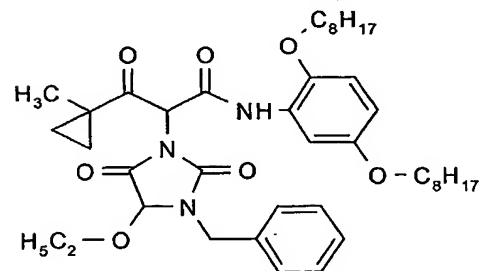
IV-37



IV-38

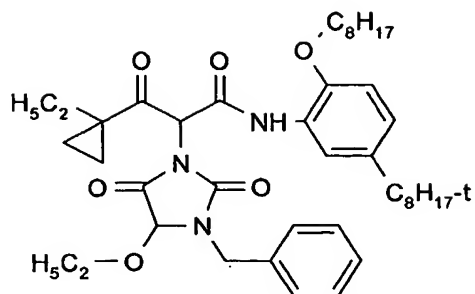


IV-39

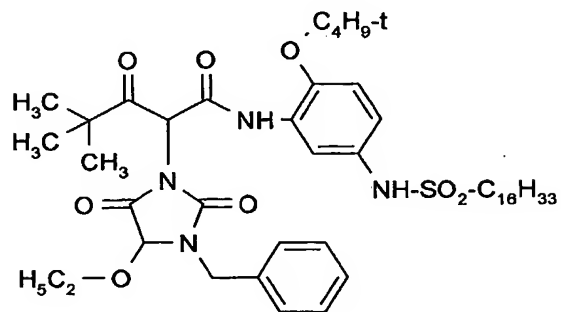


59

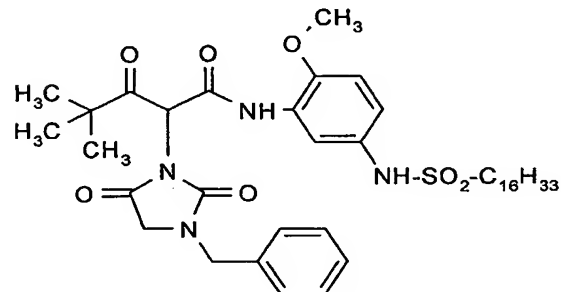
IV-40



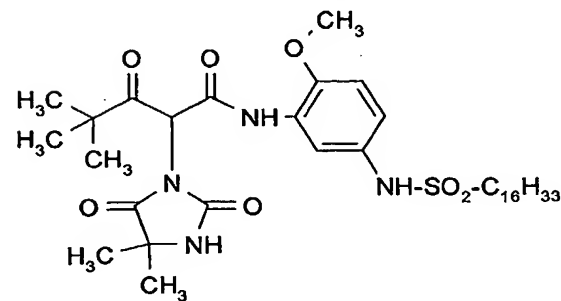
IV-41



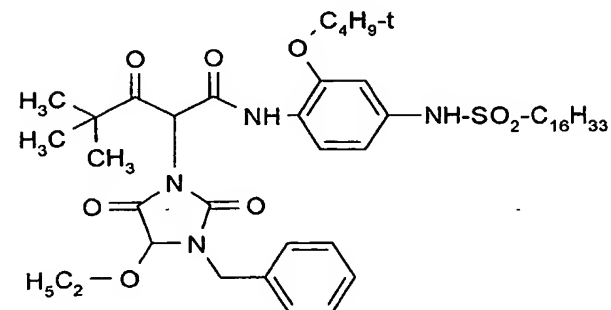
IV-42



IV-43

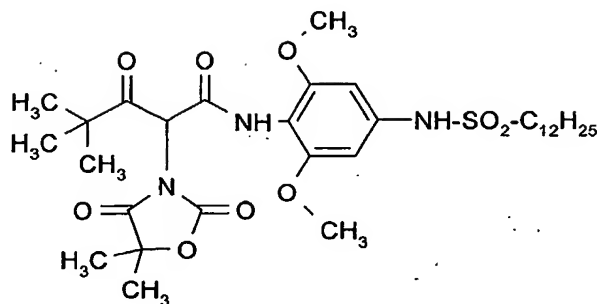


IV-44

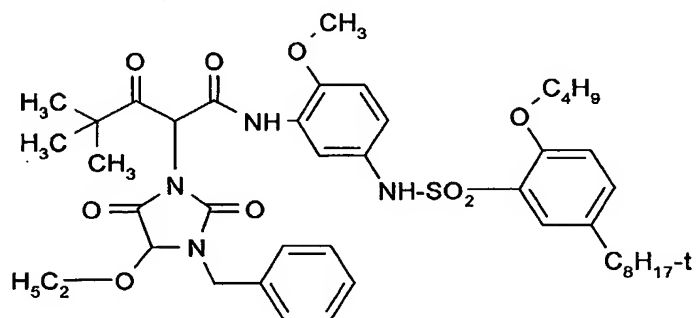


60

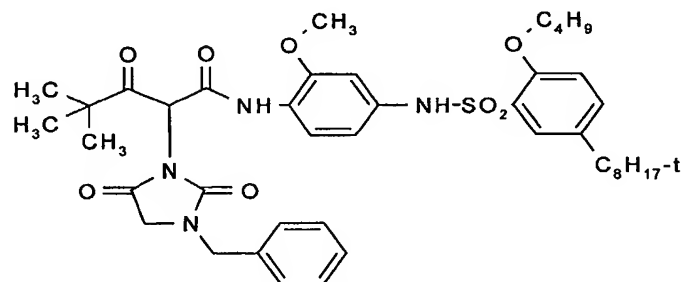
IV-45



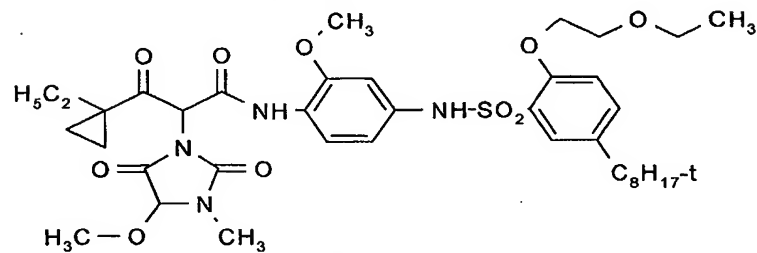
IV-46



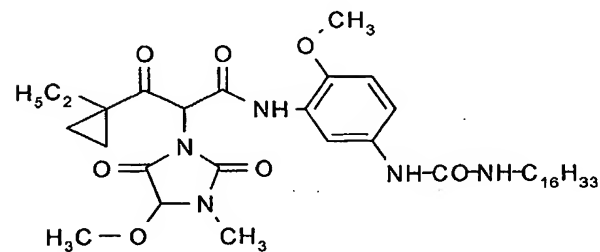
IV-47



IV-48



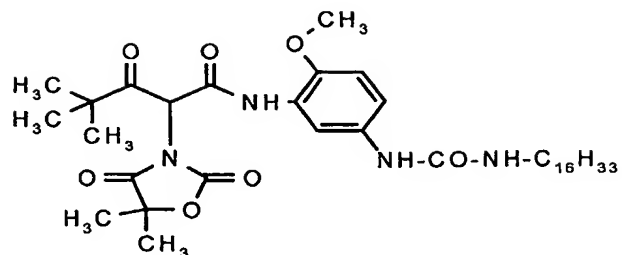
IV-49



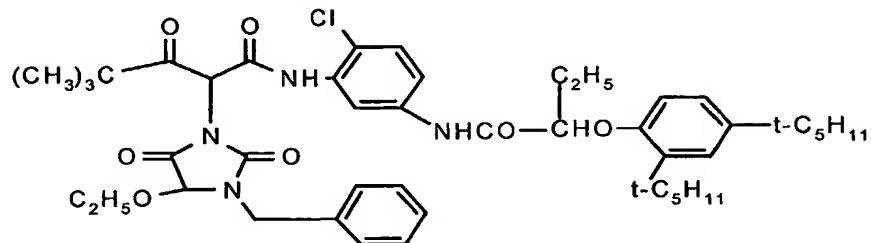


61

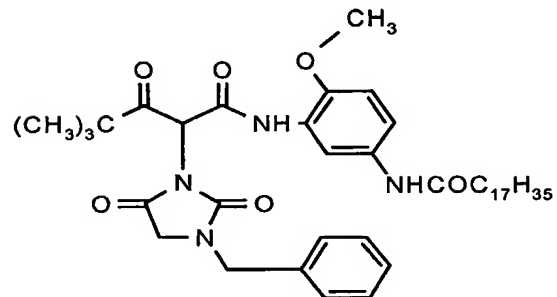
IV-50



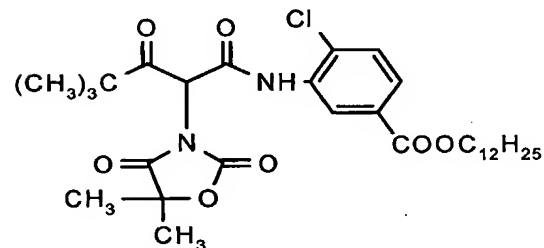
IV-51



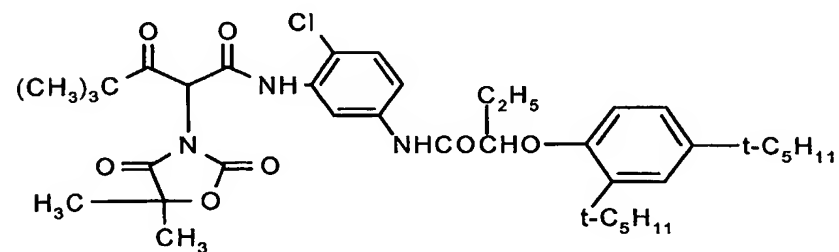
IV-52



IV-53

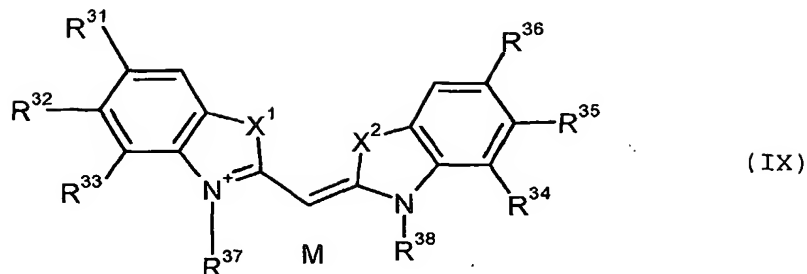


IV-54



According to a preferred embodiment of the deformable colour photographic silver halide material, according to the present invention, the blue-sensitive silver halide emulsion layer contains  
 a blue sensitizer represented by formula (IX):

62

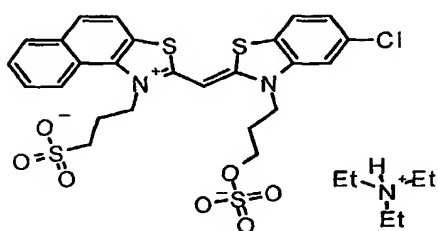


wherein  $X^1$  and  $X^2$  independently represent S or Se,  $R^{31}$  to  $R^{36}$  independently represent hydrogen, halogen or an alkyl-, alkoxy, aryl or hetero-aryl group or  $R^{31}$  and  $R^{32}$ ;  $R^{32}$  and  $R^{33}$ ;  $R^{34}$  and  $R^{35}$ ;  $R^{35}$  and  $R^{36}$  together represent the atoms necessary to form an anellated benzo-, naphtho- or heterocyclic ring,  $R^{37}$  and  $R^{38}$  independently represent an alkyl-, sulfoalkyl-, carboxyalkyl-,  $-(CH_2)_1SO_2R^{39}SO_2$ -alkyl,  $-(CH_2)_1SO_2R^{39}CO$ -alkyl,  $-(CH_2)_1COR^{39}SO_2$ -alkyl or  $-(CH_2)_1-COR^{39}CO$ -alkyl group,  $R^{39}$  represents  $-N^-$  or  $-NH-$ ,  $l$  is a whole number between 1 and 6 and  $M$  is an optional counter-ion providing charge compensation.

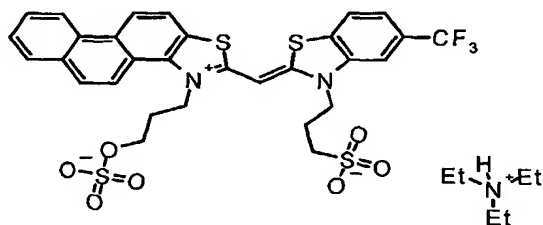
$R^{31}$  to  $R^{36}$  preferably independently represent hydrogen, F, Cl, Br or alkyl,  $CF_3$ ,  $OCH_3$  or phenyl groups; or  $R^{31}$  and  $R^{32}$ ;  $R^{32}$  and  $R^{33}$ ;  $R^{34}$  and  $R^{35}$ ; or  $R^{35}$  and  $R^{36}$  together represent the atoms necessary to form an anellated benzo- or naphtho-ring.

Particularly suitable blue sensitizers include the following compounds, in which "Et" represents Ethyl:

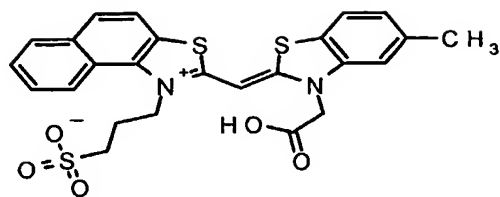
IX-1



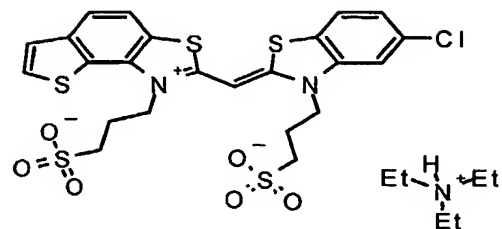
IX-2



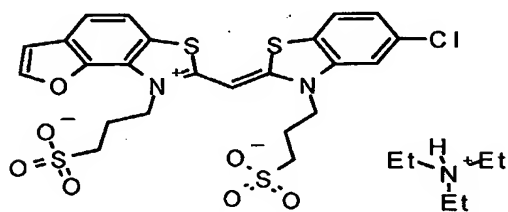
IX-3



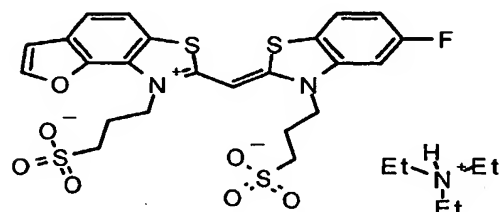
IX-4



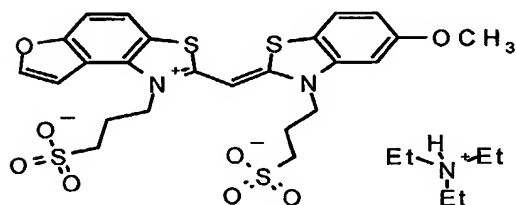
IX-5



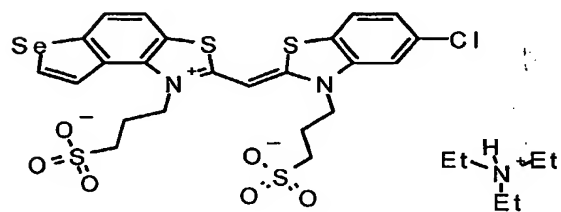
IX-6



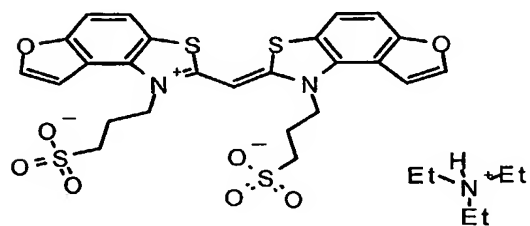
IX-7



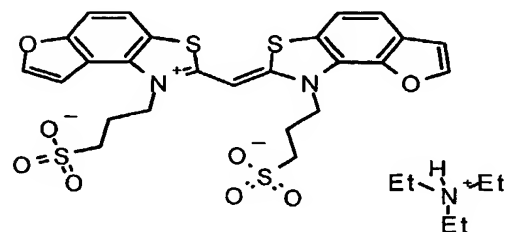
IX-8



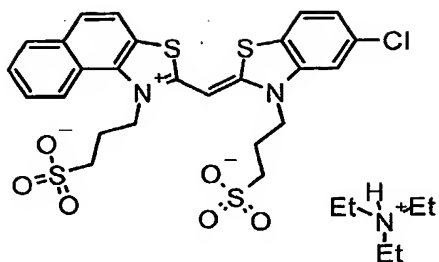
IX-9



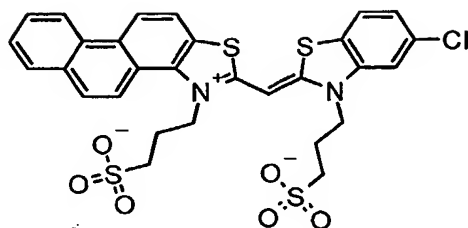
IX-10



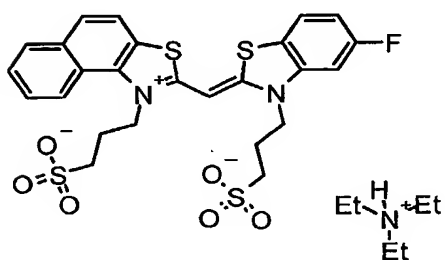
IX-11



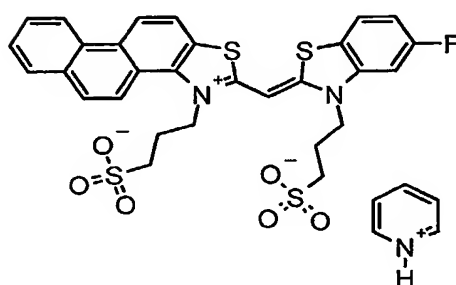
IX-12



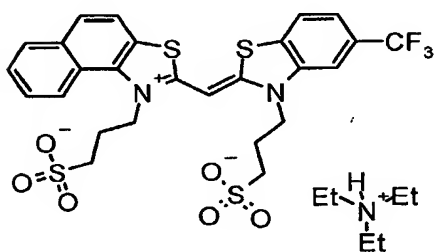
IX-13



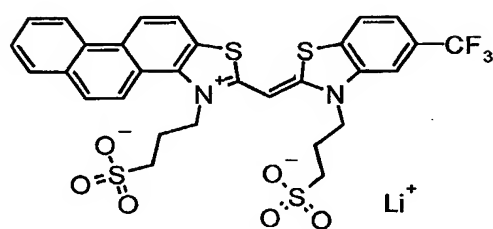
IX-14



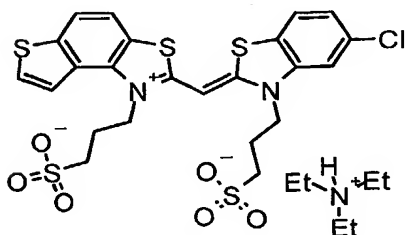
IX-15



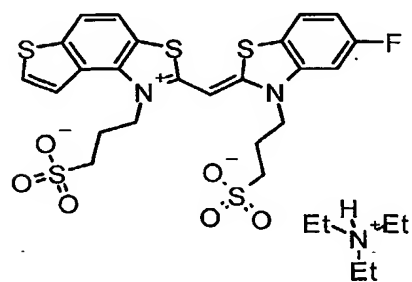
IX-16



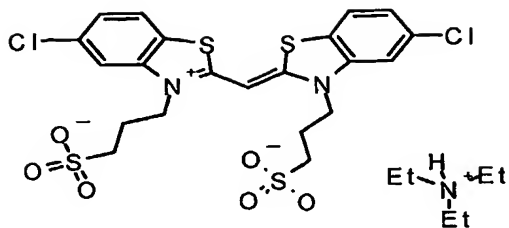
IX-17



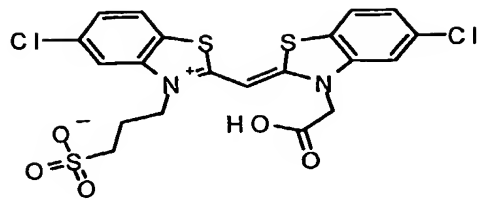
IX-18



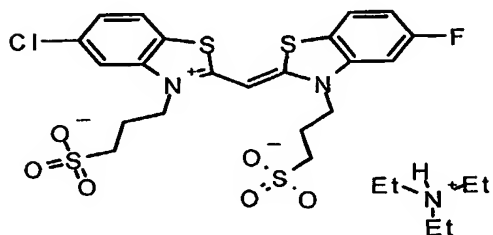
IX-21



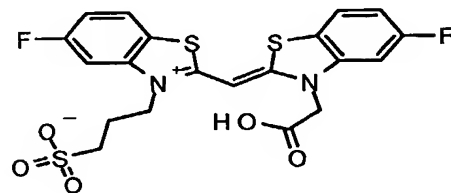
IX-22



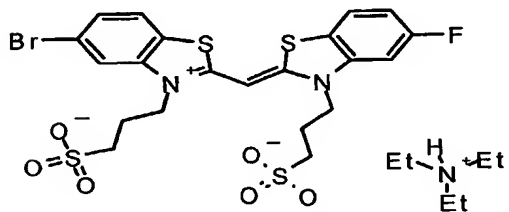
IX-23



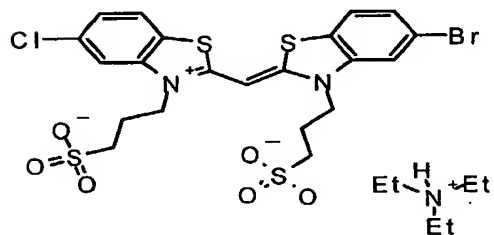
IX-24



IX-25

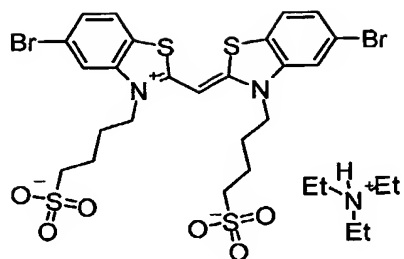


IX-26

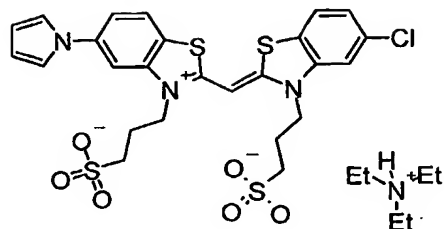


66

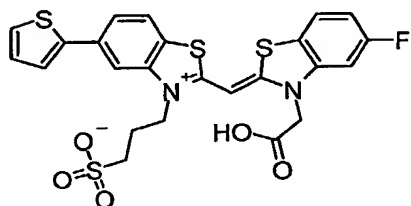
IX-27



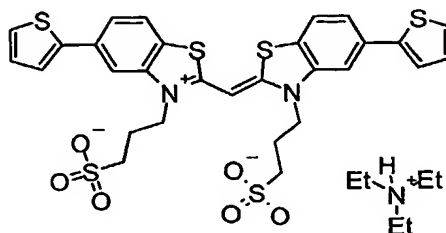
IX-28



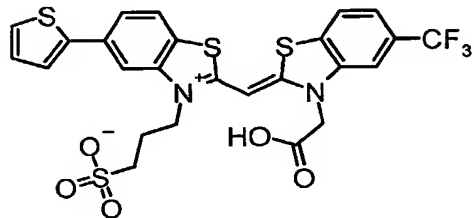
IX-29



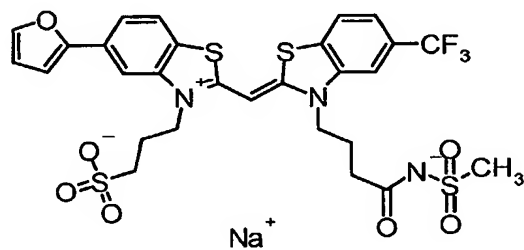
IX-30



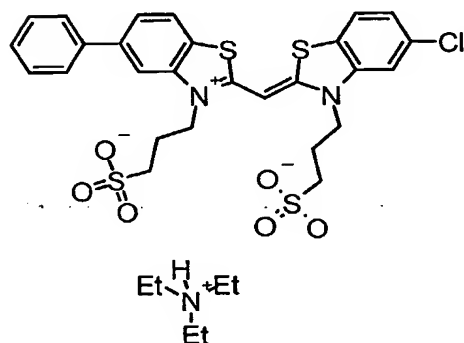
IX-31



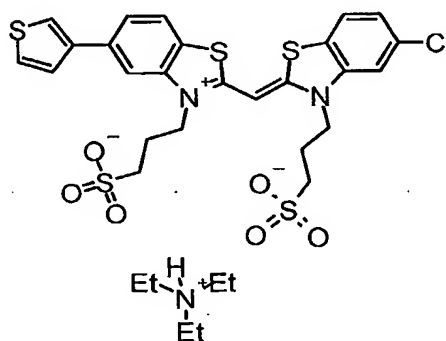
IX-32



IX-33



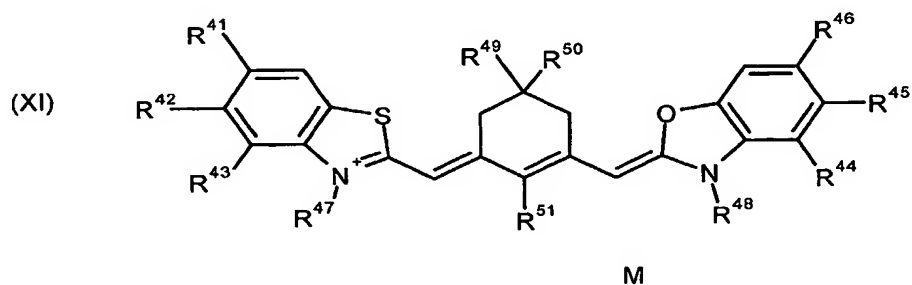
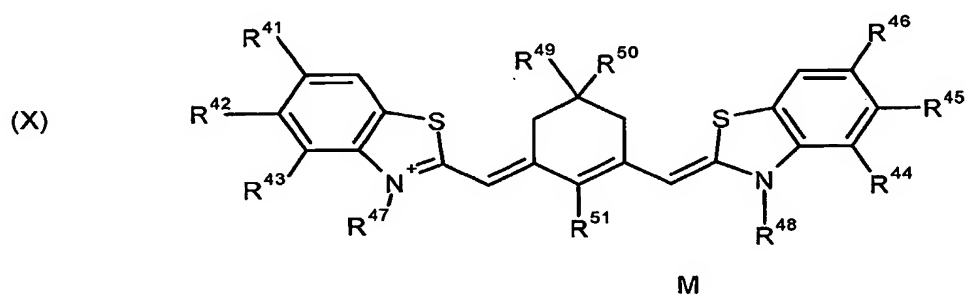
IX-34



In a preferred embodiment of the present invention, the colour  
s photographic material contains at least one blue-sensitive layer  
comprising a blue sensitizer according to formula (IX) wherein:  $X^1$

and  $X^2$  represent S,  $R^{35}$  represents a trifluormethyl group or a halogen atom, in particular a chlorine atom,  $R^{32}$  and  $R^{33}$  together represent the atoms necessary to form an anellated benzo-, naphtho- or heterocyclic ring, particularly an anellated benzo-ring and  $R^{37}$  and  $R^{38}$  independently represent sulfoalkyl-, carboxyalkyl-,  $-(CH_2)_1SO_2R^{39}SO_2$ -alkyl-,  $-(CH_2)_1SO_2R^{39}CO$ -alkyl-,  $-(CH_2)_1COR^{39}SO_2$ -alkyl-,  $-(CH_2)_1-COR^{39}CO$ -alkyl, particularly sulfoalkyl groups.

Suitable red sensitizers include compounds according to formula (X) and (XI):

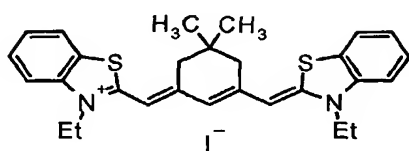


wherein  $R^{41}$  to  $R^{46}$  independently represent hydrogen, halogen or an alkyl-, alkoxy, aryl or hetero-aryl group; or  $R^{41}$  and  $R^{42}$ ;  $R^{42}$  and  $R^{43}$ ;  $R^{44}$  and  $R^{45}$ ; or  $R^{45}$  and  $R^{46}$  together represent the atoms necessary to form an anellated benzo-, naphtho- or heterocyclic ring,  $R^{47}$  and  $R^{48}$  independently represent an alkyl-, sulfoalkyl-, carboxyalkyl-,  $-(CH_2)_1SO_2YSO_2$ -alkyl-,  $-(CH_2)_1SO_2YCO$ -alkyl-,  $-(CH_2)_1COYSO_2$ -alkyl or  $-(CH_2)_1-COYCO$ -alkyl group, Y represents  $-N^-$ - or  $-NH^-$ ,  $R^{49}$  and  $R^{50}$  independently represent a hydrogen atom or an alkyl- or an aryl group,  $R^{51}$  represents a hydrogen atom, a halogen atom or an alkyl group and M represents an optional counter-ion providing charge compensation.

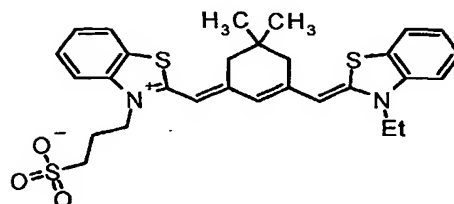
25  $R^{41}$  to  $R^{46}$  preferably independently represent hydrogen, F, Cl, Br or alkyl,  $CF_3$ ,  $OCH_3$  or phenyl groups; or  $R^{41}$  and  $R^{42}$ ;  $R^{42}$  and  $R^{43}$ ;  $R^{44}$  and  $R^{45}$ ; or  $R^{45}$  and  $R^{46}$  together represent the atoms necessary to form an anellated benzo- or naphtho-ring.

Examples of red sensitizers are given below, wherein "Et" represents Ethyl:

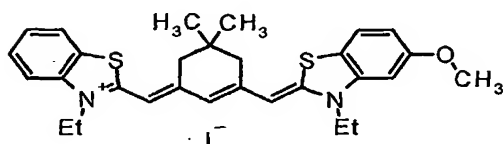
X-1



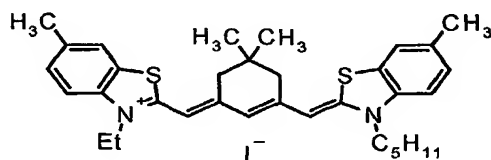
X-2



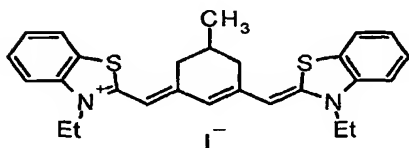
X-3



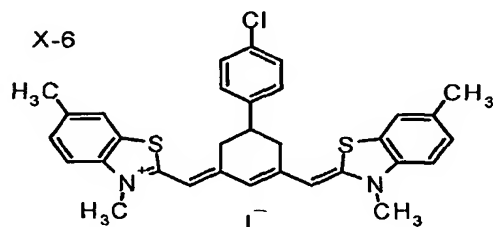
X-4



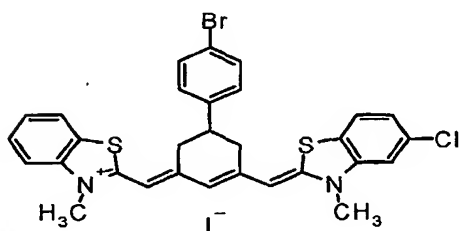
X-5



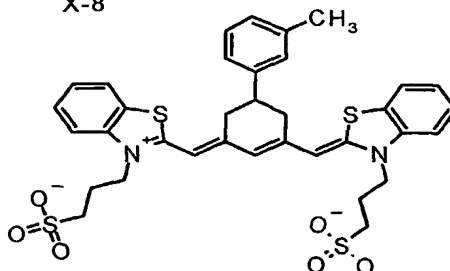
X-6



X-7



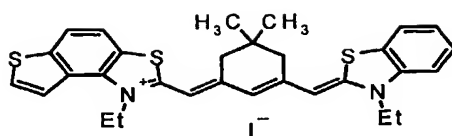
X-8



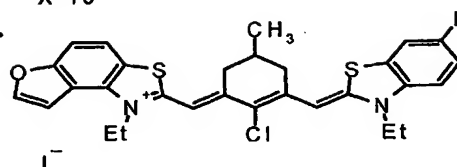


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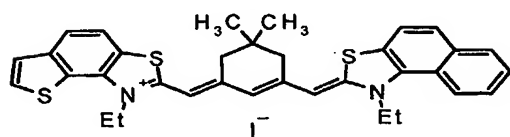
X-9



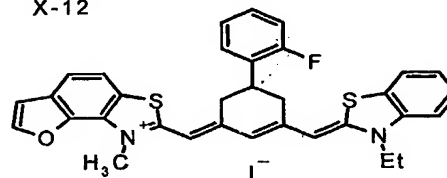
X-10



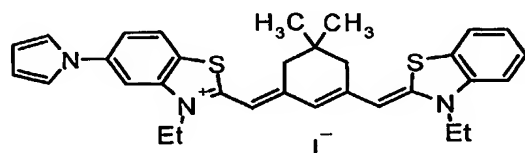
X-11



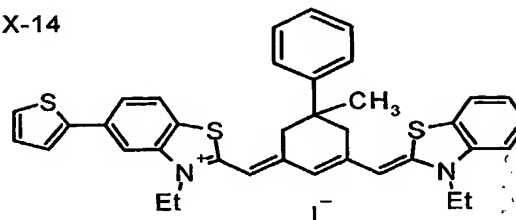
X-12



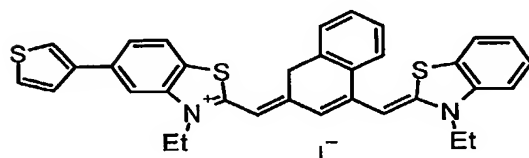
X-13



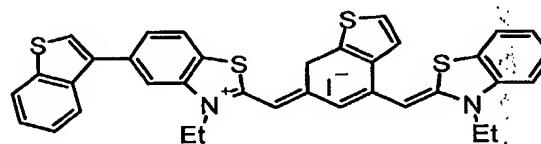
X-14



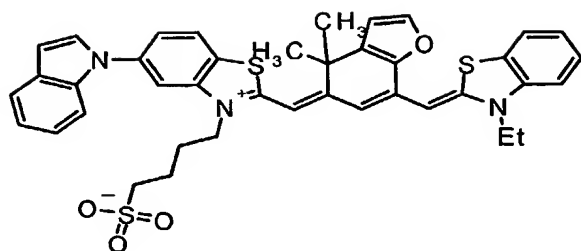
X-15



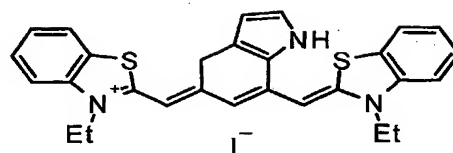
X-16



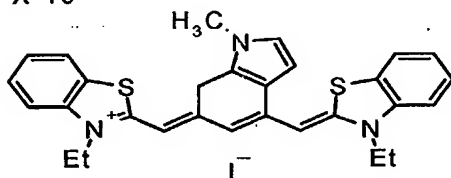
X-17



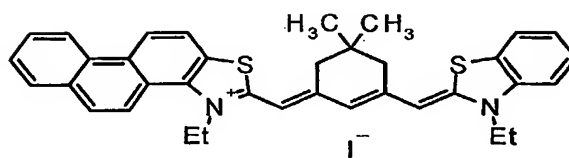
X-18



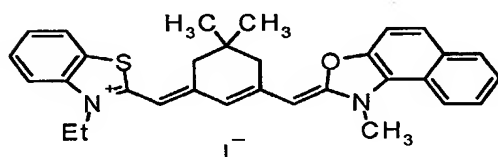
X-19



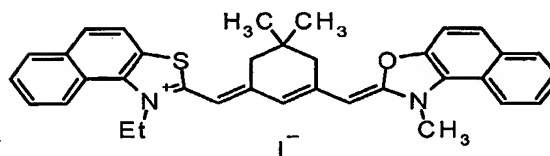
X-20



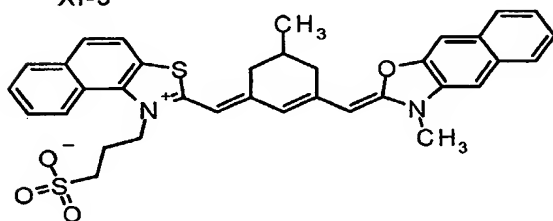
XI-1



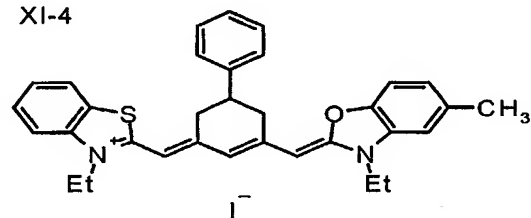
XI-2



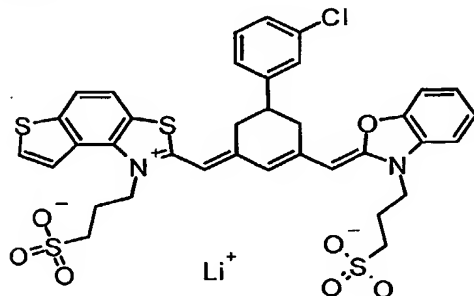
XI-3



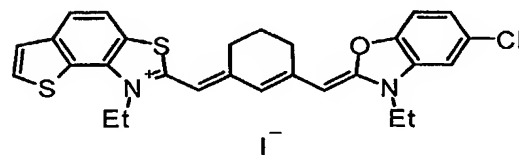
XI-4



XI-5

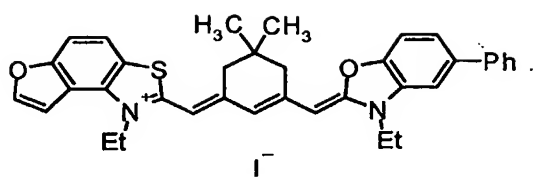


XI-6

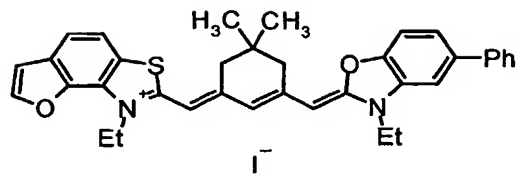


71

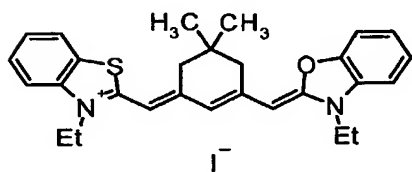
XI-7



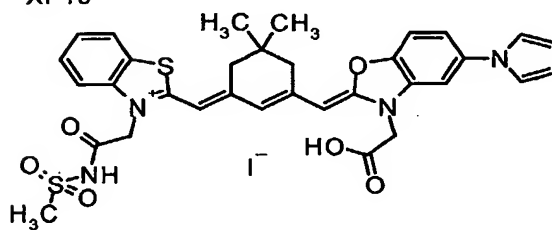
XI-8



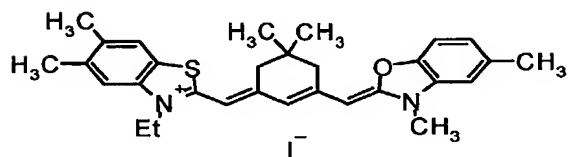
XI-9



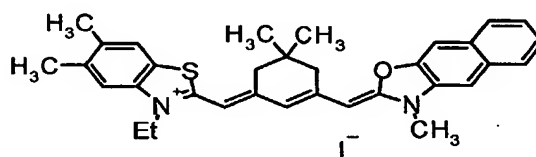
XI-10



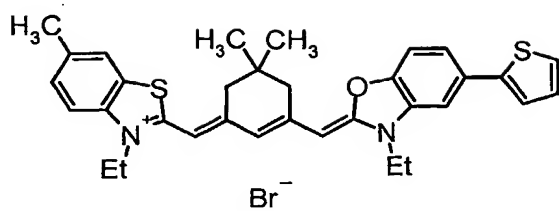
XI-11



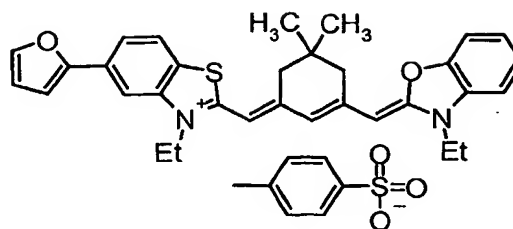
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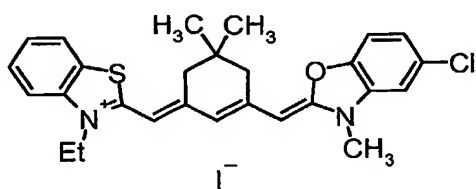
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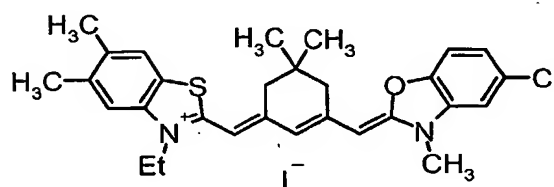
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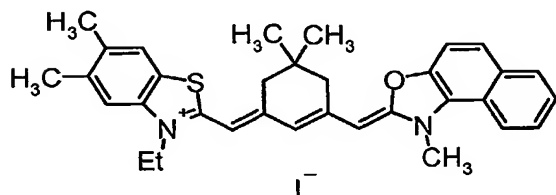
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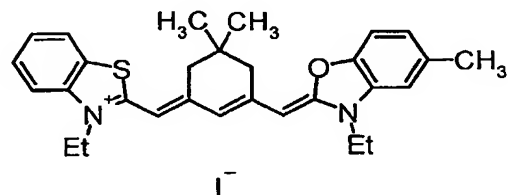
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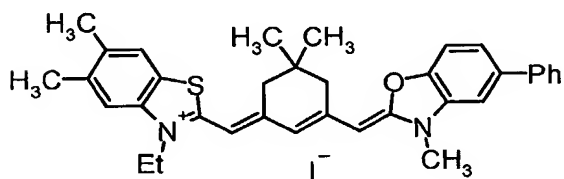
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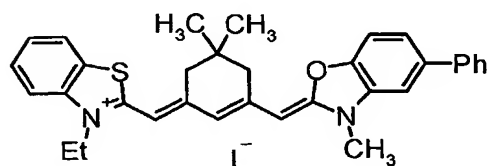
XI-18



XI-19

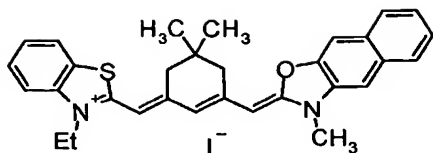


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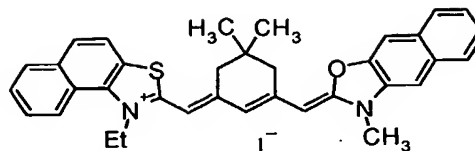


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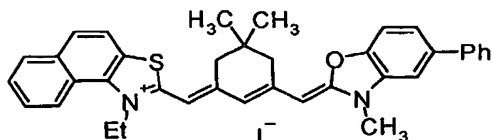
XI-21



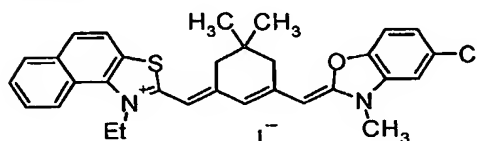
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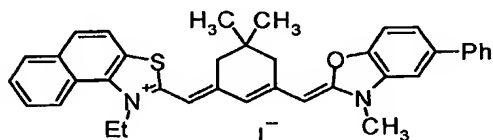
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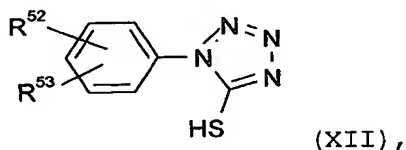
XI-24



XI-25



In a further preferred embodiment of the deformable colour photographic silver halide material, according to the present invention, the deformable colour photographic material contains a layer containing at least one compound represented by formula (XII)



10 in which  $R^{52}$  represents H,  $CH_3$  or  $OCH_3$ ;  $R^{53}$  represents H, OH,  $CH_3$ ,  $OCH_3$ ,  $NHCO-R^{54}$ ,  $COOR^{54}$ ,  $SO_2NH_2$ ,  $NHCONH_2$  or  $NHCONH-CH_3$ ; and  $R^{54}$  represents a  $C_1-C_4$ -alkyl group. Compounds according to formula (XII) are preferably present in a light-sensitive layer in a quantity of 50 to 5000 mg per kg Ag, particularly preferably in a quantity of 200 to 2000 mg per kg Ag.

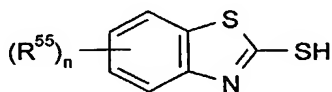
Preferred compounds according to formula (XII) are given below:

	$R^{52}$	$R^{53}$
XII-1	H	H
XII-2	H	$O-OCH_3$

	$R^{52}$	$R^{53}$
XII-3	H	m-OCH <sub>3</sub>
XII-4	H	p-OCH <sub>3</sub>
XII-5	H	o-OH
XII-6	H	m-OH
XII-7	H	p-OH
XII-8	H	m-NHCOCH <sub>3</sub>
XII-9	H	p-COOC <sub>2</sub> H <sub>5</sub>
XII-10	H	p-COOH
XII-11	H	m-NHCONH <sub>2</sub>
XII-12	H	p-SO <sub>2</sub> NH <sub>2</sub>
XII-13	o-OCH <sub>3</sub>	p-OCH <sub>3</sub>
XII-14	H	m-NHCONHCH <sub>3</sub>

In a particularly preferred embodiment of the present invention, the colour photographic material contains a compound according to formula (XII) in a blue-sensitive silver halide emulsion layer.

In a preferred embodiment of the present invention, the colour photographic material contains at least one layer containing a compound according to formula (XIII):

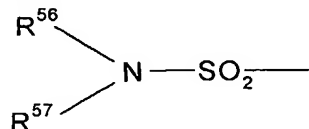


(XIII),

in which  $R^{55}$  represents a substituent and  $n$  is 1, 2 or 3. Preferably  $R^{55}$  represents a polar group, in particular a sulfo group, a sulfonate group, or a substituted or unsubstituted sulfonamido group. The sulfonamido group can be bonded through the S- or the N-atom of the group.

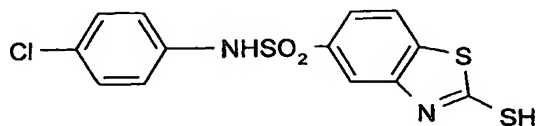
Compounds according to formula (XIII) are preferably present in a red-sensitive silver halide emulsion layer in a quantity of 100 to 5000 mg per kg Ag, particularly preferably in a quantity of 500 to 3000 mg per kg Ag.

Stabilizers according to formula (XIII) are particularly preferred in which  $R^{55}$  represents



and; R<sup>56</sup> and R<sup>57</sup> independently represent H, Cl or C<sub>1</sub>-C<sub>4</sub>-alkyl, phenyl or chlorophenyl groups.

Particularly preferred compounds according to formula (XIII) include:



(XIII-1).

In a particularly preferred embodiment of the present invention, the red-sensitive layer contains at least one compound according to formula (XII) and at least one compound according to formula (XIII).

The main ingredients of photographic emulsion layers are binders, silver halide crystals and colour couplers. Details over suitable binders are to be found in Research Disclosure 37254, part 2 (1995) page 286, herein incorporated by reference.

The mostly hydrophobic colour couplers, as well as other hydrophobic ingredients in the layer, are usually dissolved or dispersed in high boiling point organic solvents. These solutions or dispersions are then emulsified in an aqueous binder solution (usually gelatin) and remain in the layers after drying as fine droplets (0.05 to 0.8 µm in diameter).

Suitable high boiling point organic solvents, methods for incorporation in the layers of a photographic material and other methods to incorporate chemical compounds in photographic layers are to be found in Research Disclosure 37254, part 6 (1995) page 292, herein incorporated by reference.

The light-insensitive layers generally coated between the light-sensitive layers with different spectral sensitivities can contain ingredients, which hinder undesirable diffusion of developer oxidation products from one light-sensitive layer to another such layer with different spectral sensitization.

Suitable compounds (white couplers, scavengers for developer oxidation products (also called DOP scavengers, Dox scavengers, interlayer scavengers or just scavengers) are to be found in Research Disclosure 37254, part 7 (1995) page 292 and in Research Disclosure 37038, part III, page 84 herein incorporated by reference.

The colour photographic material may further contain UV-light absorbing compounds, brighteners, spacing agents, filter dyes, formaldehyde captors, anti-fading agents, antioxidants, D<sub>min</sub>-dyes, additives to improve the dye, coupler and white image area  
5 stability, additives to reduce colour fog, plasticizers (latices), biocides and polyvinylpyrrolidone. Such additives and other additives can be contained in the emulsion and interlayers, but can also be contained in additional layers between the support and emulsion layers and/or on the non-emulsion layer-bearing side of  
10 the support. Suitable compounds are to be found in Research Disclosure 37254, part 8 (1995) page 292 and in Research Disclosure 37038, parts IV, V, VI, VII, X, XI and XIII (1995), from page 84 herein incorporated by reference.

The layers of the colour photographic material are usually  
15 hardened i.e. the binders used, preferably gelatin, is crosslinked by a suitable chemical process. Immediate or fast hardeners are preferably employed. Suitable immediate and fast hardeners are to be found in Research Disclosure 37254, part 9 (1995), page 294 and in Research Disclosure 37038, part XII (1995), page 86, herein  
20 incorporated by reference.

The outermost layers of the photographic material and in particular the outermost layer on the image side can be embossed and/or coloured and/or printed with any kind of design, image or text.

#### 25 Industrial application

The process for producing a deformed image, according to the present invention, can be used to apply any kind of representations like images, designs, patterns, letters and so forth to a wide  
30 variety of work pieces including pieces of furniture.

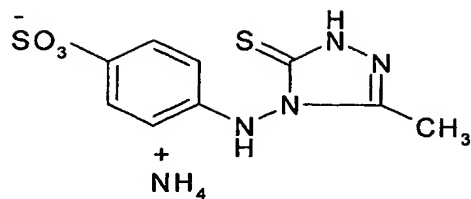
The invention is illustrated hereinafter by way of comparative and invention examples. The percentages and ratios given in these examples are by weight unless otherwise indicated.

35 The following compounds were used in the EXAMPLES:

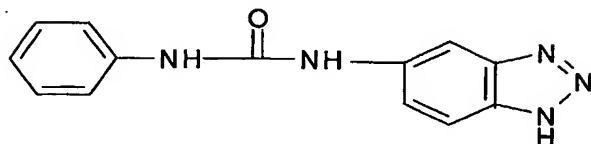


77

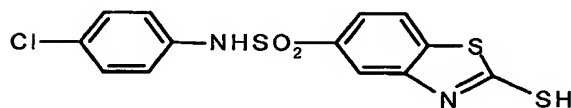
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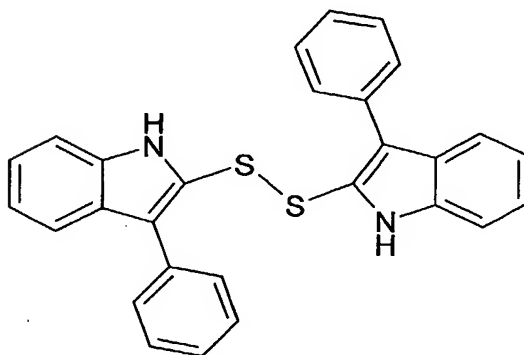
EST-3:



EST-4:

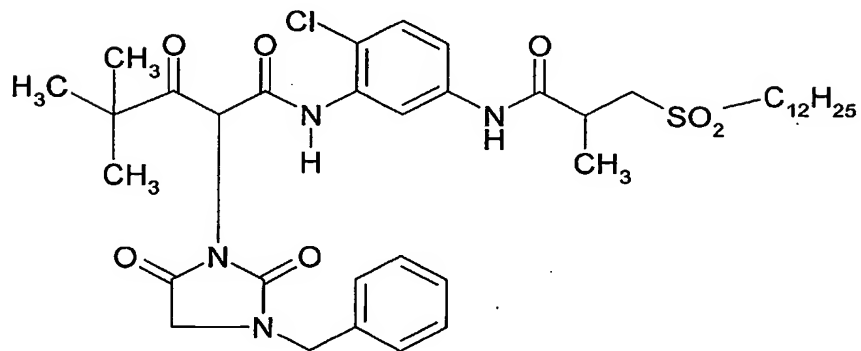


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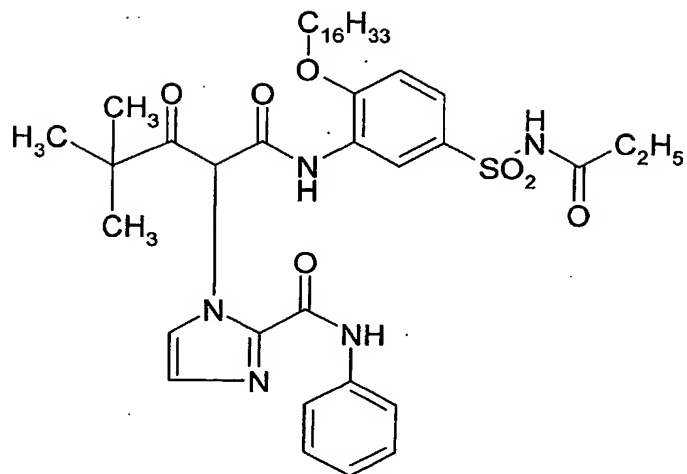


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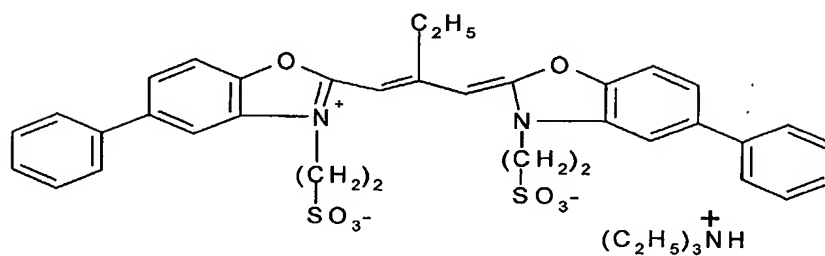
GB-1



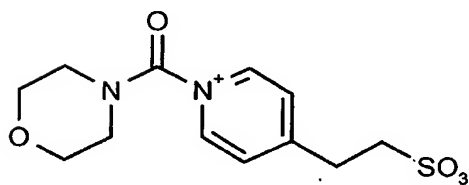
GB-3



GS-2:

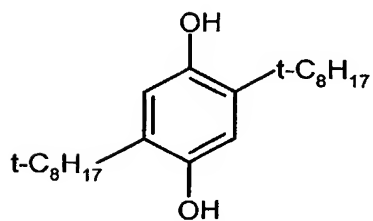


H-1

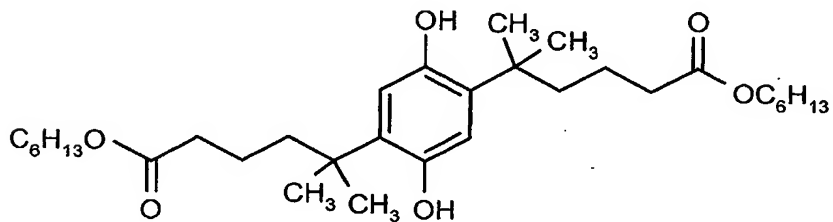


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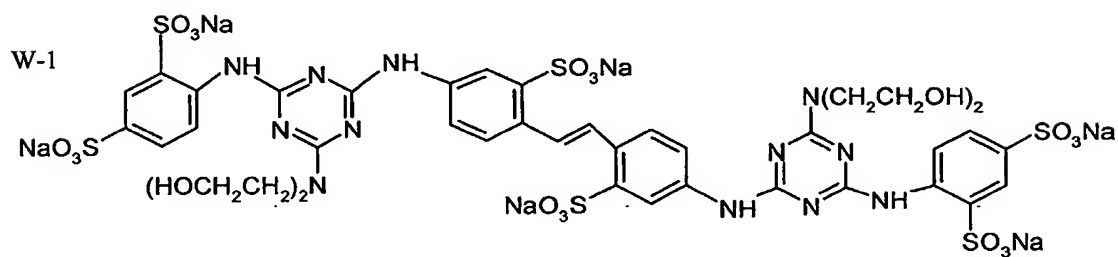
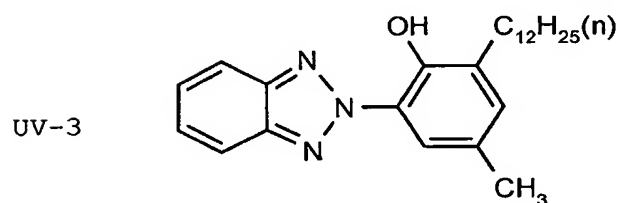
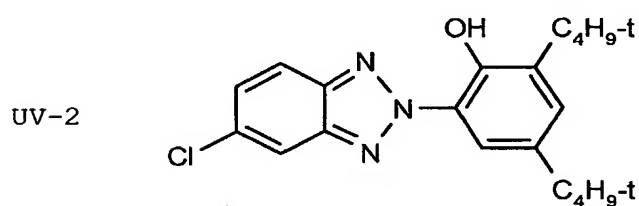
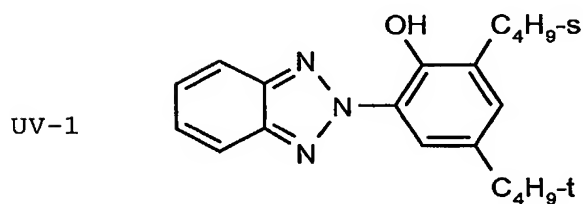
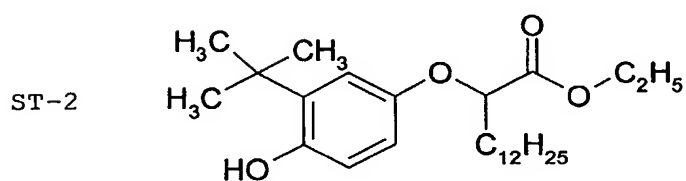
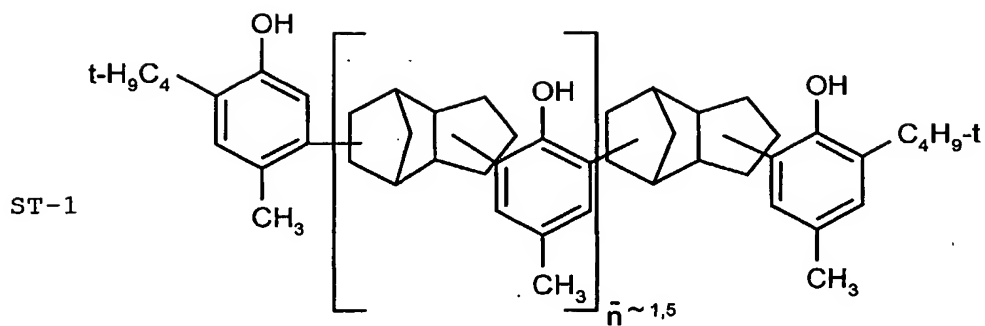
SC-1



SC-2



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## PREPARATION OF SILVER HALIDE EMULSIONS

Lippmann emulsion (EmM1):

The following solutions were prepared:

Solution 01	deionized water	1100 g
	gelatin	140 g
	n-decanol	1 g
	NaCl	4 g
Solution 02	deionized water	1860 g
	NaCl	360 g
Solution 03	deionized water	1800 g
	AgNO <sub>3</sub>	1000 g

5 Solutions 02 and 03 at 40°C were simultaneously added at a constant rate to Solution 01 in a precipitation vessel at a pAg of 7.7 and a pH of 5.3 with vigorous stirring over a period of 30 minutes. During the precipitation the pAg-value was maintained by adding a  
10 sodium chloride solution and the pH maintained by adding dilute sulphuric acid to the precipitation vessel. A silver chloride emulsion was obtained with an average silver chloride grain size of 0.09 µm. The weight ratio of gelatin to silver nitrate was 0.14. The emulsion was then subjected to ultrafiltration at 50°C  
15 and redispersed with sufficient gelatin and deionized water to yield a dispersion containing 200g of silver chloride per kg dispersion, a weight ratio of gelatin to silver nitrate (equivalent to AgX present) of 0.3 and an average silver chloride grain size of 0.13 µm.

20

Lippmann emulsion (EmM2):

Lippmann emulsion EmM2 was prepared as described for EmM1 except that Solution 04 was used instead of Solution 02.

25

Solution 04	deionized water	1860 g
	NaCl	360 g
	K <sub>2</sub> IrCl <sub>6</sub>	
		200 µg

The emulsion obtained contained 90 mol% silver chloride, 10 mol% silver bromide and  $70 \times 10^{-9}$  mol Ir<sup>4+</sup> per mol silver chloride.

30 Lippmann emulsion (EmM3):

Lippmann emulsion EmM3 was prepared as described for EmM1 except that Solution 05 was used instead of Solution 02.

Solution 05	deionized water	1860 g
	NaCl	360 g
	K <sub>2</sub> IrCl <sub>6</sub>	5680 µg

5

The emulsion obtained contained  $2000 \times 10^{-9}$  mol Ir<sup>4+</sup> per mol silver chloride.

#### BLUE-SENSITIVE EMULSIONS EmB1-EmB3:

10

##### EmB1:

The following solutions were prepared:

Solution 11	deionized water	1100 g
	gelatin	136 g
	n-decanol	1 g
	NaCl	4 g
	EmM1	36 g
Solution 12	deionized water	1860 g
	NaCl	360 g
	K <sub>2</sub> IrCl <sub>6</sub>	14.2 µg
Solution 13	deionized water	1800 g
	AgNO <sub>3</sub>	1000 g

15

Solutions 12 and 13 at 50°C were simultaneously added to Solution 11 in a precipitation vessel at a pAg of 7.7 with vigorous stirring over a period of 150 minutes. During the precipitation the pAg-value was maintained by adding a sodium chloride solution and a pH of 5.3 was maintained by adding dilute sulphuric acid to the precipitation vessel. The addition rate of both Solutions 12 and 13 was so regulated that in the first 100 minutes it increased linearly from 2 mL/min to 16 mL/min and during the final 50 minutes was held constant at 20 mL/min. A silver chloride emulsion was thereby obtained with an average silver chloride grain size of 0.85 µm. The weight ratio of gelatin to silver nitrate (equivalent to AgX) was 0.14. The emulsion was then subjected to ultrafiltration at 50°C and redispersed with sufficient gelatin and deionized water to yield a dispersion containing 200g of silver chloride per kg

20

25

dispersion and a weight ratio of gelatin to silver nitrate (equivalent to AgX present) of 0.56. The emulsion thereby obtained contained  $5 \times 10^{-9}$  mol  $\text{Ir}^{4+}$  per mole of silver chloride.

The emulsion first was prestabilized with 0.01 mmol of compound EST-6 and then was chemically ripened at a pH of 5.3 with  $0.13 \times 10^{-6}$  mol ammonium tetrachloroaurate and  $5.4 \times 10^{-6}$  mol sodium thiosulphate per mole of silver chloride for 180 minutes at a temperature of  $47^\circ\text{C}$ . After chemical ripening the following ingredients were added per mole of silver chloride at  $40^\circ\text{C}$ : 0.3 mmol of the spectral sensitizing compound (IX-1), 0.5 mmol of the stabilizing compound XII-8, 0.5 mmol of the stabilizing compound EST-1 and finally 0.6 mmol of potassium bromide.

**EmB2:**

15

The precipitation, desalting and redispersion were carried out as described for EmB1, except that  $28.4 \mu\text{g}$   $\text{K}_2\text{IrCl}_6$  was added to solution 12. The emulsion thereby obtained contained  $10 \times 10^{-9}$  mol  $\text{Ir}^{4+}$  per mole silver chloride.

20

The emulsion first was prestabilized with 0.01 mmol of compound EST-6 and then was chemically ripened at a pH of 5.3 with  $0.13 \times 10^{-6}$  mol ammonium tetrachloroaurate and  $5.4 \times 10^{-6}$  mol sodium thiosulphate per mole of silver chloride for 180 minutes at a temperature of  $47^\circ\text{C}$ . After chemical ripening the following ingredients were added per mole of silver chloride at  $40^\circ\text{C}$ : 0.3 mmol of the spectral sensitizing compound (IX-1), 0.5 mmol of the stabilizing compound XII-8, 0.5 mmol of the stabilizing compound EST-1 and finally 0.6 mmol of potassium bromide.

25

**EmB3:**

30

The emulsion is prepared by recrystallization of the Lippmann emulsion EmM2 onto the separate preprecipitate emulsion (nucleus emulsion) EmV1, which was prepared as follows:

35

**Preparation of the preprecipitate emulsion EmV1:**

The precipitation, desalting and redispersion were carried out as described for EmB1, except that the amount of EmM1 added to solution 11 was increased to 40 g. A silver chloride emulsion was thereby obtained with an average silver chloride grain size of  $0.82 \mu\text{m}$ .

40

**Preparation of EmB3:**

1.5 kg of EmV1 (representing 300 g AgNO<sub>3</sub>) melted at 40°C in a precipitation vessel while stirring. In a separate vessel 0.25 kg of Lippmann emulsion EmM2 (representing 50 g AgNO<sub>3</sub>) was melted at 40°C while stirring. Under vigorous stirring, 25 ml of a 20 % by weight NaCl solution was added to EmV1. After a digestion of 5 minutes EmM2 is added to EmV1 within 50 minutes at a constant rate. After a digestion of 10 minutes the emulsion was then redispersed with sufficient gelatin and deionized water to yield a weight ratio of gelatin to silver nitrate (equivalent to AgX present) of 0.56. A silver chloride emulsion was thereby obtained with an average silver chloride grain size of 0.85 µm. The emulsion thereby obtained contained  $10 \times 10^{-9}$  mol Ir<sup>4+</sup> per mole of silver chloride.

The emulsion first was prestabilized with 0.01 mmol of compound EST-6 and then was chemically ripened at a pH of 5.3 with  $0.13 \times 10^{-6}$  mol ammonium tetrachloroaurate and  $5.4 \times 10^{-6}$  mol sodium thiosulphate per mole of silver chloride for 180 minutes at a temperature of 47°C. After chemical ripening the following ingredients were added per mole of silver chloride at 40°C: 0.3 mmol of the spectral sensitizing compound (IX-1), 0.5 mmol of the stabilizing compound XII-8, 0.5 mmol of the stabilizing compound EST-1 and finally 0.6 mmol of potassium bromide.

GREEN-SENSITIVE EMULSIONS EmG1-EmG3:

EmG1:

The following solutions were prepared:

Solution 21	deionized water	1100 g
	gelatin	136 g
	n-decanol	1 g
	NaCl	4 g
	EmM1	195 g
Solution 22	deionized water	1860 g
	NaCl	360 g
	K <sub>2</sub> IrCl <sub>6</sub>	14.2 µg
	RhCl <sub>3</sub> .3H <sub>2</sub> O	3.8 µg
Solution 23	deionized water	1800 g
	AgNO <sub>3</sub>	1000 g

Solutions 22 and 23 at 48°C were simultaneously added to Solution 21 in a precipitation vessel at a pAg of 7.7 with intensive

stirring over a period of 75 minutes. During the precipitation the pAg-value was maintained by adding a sodium chloride solution and a pH-value of 5.3 was maintained by adding dilute sulphuric acid to the precipitation vessel. The addition rate of both solutions 22 and 23 was so regulated that in the first 50 minutes it increased linearly from 4 mL/min to 36 mL/min and during the final 25 minutes was held constant at 40 mL/min. A silver chloride emulsion was thereby obtained with an average silver chloride grain size of 0.50  $\mu\text{m}$ . The weight ratio of gelatin to silver nitrate (equivalent to 10 AgX) was 0.14. The emulsion was then subjected to ultrafiltration at 50°C, washed and redispersed with sufficient gelatin and deionized water to yield a dispersion containing 200g of silver chloride per kg dispersion,  $5 \times 10^{-9}$  mol  $\text{Ir}^{4+}$  and  $2.5 \times 10^{-9}$  mol  $\text{Rh}^{3+}$  per mol silver chloride and a weight ratio of gelatin to silver 15 nitrate (equivalent to AgX present) of 0.56.

The emulsion was then chemically ripened at a pH of 6.0 with  $0.82 \times 10^{-6}$  mol ammonium tetrachloroaurate and  $2.74 \times 10^{-6}$  mol sodium thiosulphate per mole of silver chloride for 240 minutes at a temperature of 45°C. After chemical ripening the following 20 ingredients were added per mole AgCl at 40°C: 0,6 mmol of the green sensitizing compound (GS-2), 2.4 mmol of the stabilizing compound EST-3, 1.2 mmol of the stabilizing compound (EST-1), 0,6 mmol of the stabilizing compound (XII-1) and finally 3 mmol of potassium bromide.

25  
**EmG2:**

The precipitation, desalting and redispersion were carried out as described for EmG1 except that the amount of  $\text{K}_2\text{IrCl}_6$  in Solution 30 22 was increased from 14,2  $\mu\text{g}$  to 284  $\mu\text{g}$ . The emulsion thereby obtained contained  $100 \times 10^{-9}$  mol  $\text{Ir}^{4+}$  per mole silver chloride.

The emulsion was then chemically ripened at a pH of 6.0 with  $0.574 \times 10^{-6}$  mol ammonium tetrachloroaurate and  $1,92 \times 10^{-6}$  mol sodium thiosulphate per mole of silver chloride for 240 minutes at 35 a temperature of 45°C. After chemical ripening the following ingredients were added per mole AgCl at 40°C: 0,6 mmol of the green sensitizing compound (GS-2), 2.4 mmol of the stabilizing compound EST-3, 1.2 mmol of the stabilizing compound (EST-1), 0,6 mmol of the stabilizing compound (XII-1) and finally 3 mmol of potassium 40 bromide.



**EmG3:**

The emulsion is prepared by recrystallization of the Lippmann emulsion EmM3 onto the separate preprecipitate emulsion (nucleus emulsion) EmV2, which was prepared as follows:

Preparation of the preprecipitate emulsion EmV2:

The precipitation, desalting and redispersion were carried out as described for EmG1, except that the amount of EmM1 added to  
10 solution 21 was increased to 250 g. A silver chloride emulsion was thereby obtained with an average silver chloride grain size of 0.46  $\mu\text{m}$ .

Preparation of EmG3:

15 1.5 kg of EmV2 (representing 300 g  $\text{AgNO}_3$ ) melted at 40°C in a precipitation vessel while stirring. In a separate vessel 0.5 kg of Lippmann emulsion EmM3 (representing 100 g  $\text{AgNO}_3$ ) was melted at 50°C while stirring. Under vigorous stirring, 25 ml of a 20 % by weight NaCl solution was added to EmV2. After a digestion of 5  
20 minutes EmM3 is added to EmV2 within 80 minutes at a constant rate. After a digestion of 10 minutes the emulsion was then redispersed with sufficient gelatin and deionized water to yield a weight ratio of gelatin to silver nitrate (equivalent to AgX present) of 0.56. A silver chloride emulsion was thereby obtained with an average  
25 silver chloride grain size of 0.51  $\mu\text{m}$ . The emulsion thereby obtained contained  $504 \times 10^{-9}$  mol  $\text{Ir}^{4+}$  and 0.625 nmol  $\text{Rh}^{3+}$  per mole of silver chloride.

The emulsion was then chemically ripened at a pH of 6.0 with  $0.33 \times 10^{-6}$  mol ammonium tetrachloroaurate and  $1.10 \times 10^{-6}$  mol sodium  
30 thiosulphate per mole of silver chloride for 240 minutes at a temperature of 45°C. After chemical ripening the following ingredients were added per mole AgCl at 40°C: 0,6 mmol of the green sensitizing compound (GS-2), 2.4 mmol of the stabilizing compound EST-3, 1.2 mmol of the stabilizing compound (EST-1), 0,6 mmol of  
35 the stabilizing compound (XII-1) and finally 3 mmol of potassium bromide.

**RED-SENSITIVE EMULSIONS EmR1-EmR3:****EmR1:**

40

The precipitation, desalting and redispersion were carried out as described for EmG2. The emulsion was chemically ripened at a pH of

5.0 with  $2.2 \times 10^{-6}$  mol ammonium tetrachloroaurate and  $9.0 \times 10^{-6}$  mol sodium thiosulphate per mole silver chloride for 280 minutes at a temperature of  $65^{\circ}\text{C}$ . After chemical ripening the following ingredients were added per mole AgCl at  $40^{\circ}\text{C}$ : 75  $\mu\text{mol}$  of the spectral sensitizing compound (X-1), 2.5 mmol of the stabilizing compound EST-4 and finally 3 mmol of potassium bromide. The emulsion thereby obtained contained  $5 \times 10^{-9}$  mol  $\text{Ir}^{4+}$  and  $2.5 \times 10^{-9}$  mol  $\text{Rh}^{3+}$  per mole silver chloride.

10 **EmR2:**

The precipitation, desalting and redispersion were carried out as described for EmR1, except that 142  $\mu\text{g}$   $\text{K}_2\text{IrCl}_6$  and 3.8  $\mu\text{g}$   $\text{RhCl}_3 \times 3 \text{H}_2\text{O}$  were added to solution 22. The emulsion was chemically ripened at a pH of 5.0 with  $1.32 \times 10^{-6}$  mol ammonium tetrachloroaurate and  $9.0 \times 10^{-6}$  mol sodium thiosulphate per mole silver chloride for 280 minutes at a temperature of  $65^{\circ}\text{C}$ . After chemical ripening the following ingredients were added per mole AgCl at  $40^{\circ}\text{C}$ : 75  $\mu\text{mol}$  of the spectral sensitizing compound (X-1), 2.5 mmol of the stabilizing compound EST-4 and finally 3 mmol of potassium bromide. The emulsion thereby obtained contained  $50 \times 10^{-9}$  mol  $\text{Ir}^{4+}$  and  $2.5 \times 10^{-9}$  mol  $\text{Rh}^{3+}$  per mole silver chloride.

**EXAMPLE 1**

25

A colour photographic material, suitable for photographic processing, was prepared by coating the following layers in the following order onto a PVC plastic foil. The silver halide coverage is given as equivalent quantities of silver nitrate.

30

**LAYER ASSEMBLY 111:**

Support: 220  $\mu\text{m}$  thick PVC toned white with  $\text{TiO}_2$  (comprising no plastizisers).- corona pretreated

Subbing layer: 0.4  $\text{g}/\text{m}^2$  gelatin  
1.5  $\text{ml}/\text{m}^2$  40 % aqueous dispersion of dispersion D-1  
6.0  $\text{ml}/\text{m}^2$  30 % aqueous dispersion of colloidal silica (average particle size 0.025  $\mu\text{m}$ , pH of 8)  
0.1  $\text{ml}/\text{m}^2$  5 % aqueous solution of wetting agent Tergitol® 4 (supplied by Niacet Corporation)  
0.1  $\text{g}/\text{m}^2$  silane SL-1

26.0 g/m<sup>2</sup> deionized water

- Layer 2: (blue-sensitive layer)  
Blue-sensitized silver halide emulsion EmB1 (99,94 mol-% chloride, 0.06 mol-% bromide, average grain size 0.85  $\mu$ m) equivalent to 0.48 g/m<sup>2</sup> AgNO<sub>3</sub>  
1.00 g/m<sup>2</sup> gelatin  
0.20 g/m<sup>2</sup> yellow coupler GB-1  
0.40 g/m<sup>2</sup> yellow coupler GB-3  
0.30 g/m<sup>2</sup> tricresylphosphate (TKP)  
0.10 g/m<sup>2</sup> stabilizer ST-1
- Layer 3: (interlayer)  
1.00 g/m<sup>2</sup> gelatin  
0.06 g/m<sup>2</sup> Dox-scavenger SC-1  
0.06 g/m<sup>2</sup> Dox-scavenger SC-2  
0.12 g/m<sup>2</sup> TKP
- Layer 4: (green-sensitive layer)  
Green-sensitized silver halide emulsion EmG1 (99 mol-% chloride, 1 mol-% bromide, average grain size 0.37  $\mu$ m) equivalent to 0.35 g/m<sup>2</sup> AgNO<sub>3</sub>.  
0.76 g/m<sup>2</sup> gelatin  
0.44 g/m<sup>2</sup> magenta coupler XIV-43  
0.07 g/m<sup>2</sup> stabilizer ST-2  
0.14 g/m<sup>2</sup> stabilizer SC-2  
0.18 g/m<sup>2</sup> TKP
- Layer 5: (UV-protection layer)  
1.05 g/m<sup>2</sup> gelatin  
0.35 g/m<sup>2</sup> UV-Absorber UV-1  
0.20 g/m<sup>2</sup> UV-Absorber UV-2  
0.13 g/m<sup>2</sup> UV-Absorber UV-3  
0.06 g/m<sup>2</sup> Dox-scavenger SC-1  
0.06 g/m<sup>2</sup> Dox-scavenger SC-2  
0.33 g/m<sup>2</sup> TKP
- Layer 6: (red-sensitive layer)  
Red-sensitized silver halide emulsion EmR1 (99.0 mol-% chloride, 1 mol-% bromide, average grain size 0.37  $\mu$ m) equivalent to 0.33 g/m<sup>2</sup> AgNO<sub>3</sub>  
0.81 g/m<sup>2</sup> gelatin

0.42 g/m<sup>2</sup> cyan coupler VII-2  
 0.20 g/m<sup>2</sup> TKP  
 0.20 g/m<sup>2</sup> dibutyl phthalate

Layer 7: (UV-protection layer)  
 0.54 g/m<sup>2</sup> gelatin  
 0.35 g/m<sup>2</sup> UV-Absorber UV-1  
 0.10 g/m<sup>2</sup> UV-Absorber UV-2  
 0.05 g/m<sup>2</sup> UV-Absorber UV-3  
 0,15 g/m<sup>2</sup> TKP

Layer 8: (protective layer)  
 0.90 g/m<sup>2</sup> gelatin  
 0.05 g/m<sup>2</sup> brightener W-1  
 0.07 g/m<sup>2</sup> polyvinylpyrrolidone  
 1.20 ml/m<sup>2</sup> silicon oil  
 2.50 mg/m<sup>2</sup> spacing agent of poly(methylmethacrylate),  
 average particle size 0.8 µm  
 0.30 g/m<sup>2</sup> immediate hardening agent H-1

#### EXAMPLES 2 to 9

The layer assemblies of the colour photographic materials of  
 s EXAMPLES 2 to 9 with layer assemblies of 112, 113, 121 to 123 and  
 131 to 133 respectively were prepared analogously to that of  
 EXAMPLE 1 except the differences that are summarized in Table 1:

Table 1:

Layer assembly	Support*)	Emulsio n			Comment
		Layer 2	Layer 4	Layer 6	
111	A	EmB1	EmG1	EmR1	Comparison EXAMPLE 1
112	A	EmB2	EmG2	EmR2	INVENTION EXAMPLE 2
113	A	EmB3	EmG3	EmR2	INVENTION EXAMPLE 3
121	B	EmB1	EmG1	EmR1	Comparison EXAMPLE 4
122	B	EmB2	EmG2	EmR2	INVENTION EXAMPLE 5
123	B	EmB3	EmG3	EmR2	INVENTION EXAMPLE 6
131	C	EmB1	EmG1	EmR1	Comparison EXAMPLE 7
132	C	EmB2	EmG2	EmR2	INVENTION EXAMPLE 8

133	C	EmB3	EmG3	EmR2	INVENTION EXAMPLE 9
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\*)Support A: 220  $\mu\text{m}$  thick PVC toned white with  $\text{TiO}_2$  (comprising no plastizisers) - corona pretreated

\*)Support B: PC foil (175  $\mu\text{m}$  thick; supplied by General Electric) -  
s corona pretreated

\*)Support C: 220  $\mu\text{m}$  thick PVC toned white with  $\text{TiO}_2$  (comprising plastizisers) - corona pretreated

Table 2 gives the quantity of iridium dopant and the preparation  
10 method used for the silver halide emulsion layers given in Table 1.  
The Ir-quantities are molar ratios with respect to silver halide.

Table 2:

Layer assem- bly	Emulsions					
	Layer 2		Layer 4		Layer 6	
	Ir- quantity	Preparation method	Ir- quantity	Preparation method	Ir- quantity	Preparation method
111 121 131	5	Double jet	5	Double jet	5	Double jet
112 122 132	10	Double jet	100	Double jet	50	Double jet
113 123 133	10	Mikrat recrystal- lization	504	Mikrat recrystal- lization	50	Mikrat recrystal- lization

15

Chemical processing of photographic materials of EXAMPLES 1 to 9

All the EXAMPLES were processed as follows:

20 a) developed for 45 s at 35°C with a colour developer with the  
following composition:

9.0 g triethanolamine  
4.0 g N,N-diethylhydroxylamine  
0.05 g diethylenglycol  
5.0 g 3-methyl-4-amino-N-ethyl-N-methansulfonamidoethyl-

anilin-sulphate  
0.2 g potassium sulphite  
0.05 g triethylenglycol  
22 g potassium carbonate  
0.4 g potassium hydroxide  
2.2 g ethylenediamine-tetra-acetic acid disodium salt  
2.5 g potassium chloride  
0.3 g 1,2-dihydroxybenzol-3,4,6-trisulfonic acid  
trisodium salt

made up with water to 1000 mL; pH = 10.0

b) bleaching/fixing for 45 s at 35°C with a bleacher/fixer bath with the  
5 following composition:

75 g ammonium thiosulphate  
13.5 g sodium hydrogen sulphite  
2.0 g ammonium acetate  
57 g ethylene-diamine-tetra-acetic acid iron ammonium salt  
9.5 g 25% aqueous ammonia

made up with acetic acid to 1000 mL; pH = 5.5

c) washing with deionized water at 33°C for 2 minutes

10

d) drying

Evaluation of sensitometric properties of colour photographic materials of  
EXAMPLES 1 to 9

15

The sensitometric evaluation results obtained by digital laser  
exposure are presented in Table 3 in the form of the following  
parameters:

20 Dmin :

Minimum density of the one day old material  
without exposure according to X-Rite Status A for  
the yellow layer (Dmin Y), the magenta layer (Dmin M) and the cyan  
layer (Dmin C).

Gamma-value G3: shoulder gradation x 100, i.e. 100 times the slope  
of the sensitometric curve between a density of  
 $D_{min} + 1.60$  and a density of  $D_{min} + 2.15$  of the one

day old material according to X-Rite Status A for the yellow layer (G3 Y), the magenta layer (G3 M) and the cyan layer (G3 C).

One day old material means, that the unexposed and unprocessed material was stored for one day at a temperature of 25°C without controlling the relative humidity. This is done to get better  
5 reproducible results.

#### EXPOSURE:

The sensitometric properties of the colour photographic material  
10 were determined upon digital exposure by exposing it with an digital printer with the following technical specifications:

Red laser: wavelength of 683 nm  
Green laser: wavelength of 543 nm  
15 Blue laser: wavelength of 458 nm  
Optical resolution: 400 dpi  
Exposure time: approx. 131 ns per pixel (pixel exposure time)  
Number of colour steps attained: 256 per channel

20 First an area of the sample was so exposed at an pixel exposure time of 131 ns with an intensity I, that the density D after processing was ca. 0.6 (according to X-Rite Status A). Then the light intensity was so reduced or increased that the logarithm of the exposure,  
25  $\log(I \times t)$  was 0.1 lower or 0.1 higher than the previous exposure step. This procedure was followed until in total 29 steps were exposed. The lowest step corresponded to a zero light intensity (Dmin).

30

#### STORAGE STABILITY TEST:

A part of the freshly prepared unexposed and unprocessed material was stored for 4 weeks at 37°C without controlling the relative  
35 humidity. Following the material was exposed, processed and sensitometrically evaluated as described above. Table 4 gives for each example the difference of Dmin after storage minus Dmin of the

one day old material as  $\Delta D_{min}$  values and the difference of G3 after storage minus G3 of the one day old material as  $\Delta G3$  values.

#### SENSITOMETRIC AND STABILITY RESULTS

5

The sensitometric results of the one day old layer assemblies are summarized in table 3.

Table 3:

10

Layer assembly	Dmin			G3		
	Y	M	C	Y	M	C
111	0,135	0,137	0,124	*)	1,15	1,36
112	0,122	0,135	0,119	1,02	1,98	2,86
113	0,114	0,129	0,118	1,32	2,10	2,89
121	0,138	0,132	0,130	*)	1,18	1,43
122	0,130	0,128	0,125	1,15	2,03	2,78
123	0,124	0,124	0,120	1,28	2,11	2,90
131	0,143	0,143	0,141	*)	1,13	1,32
132	0,136	0,139	0,133	1,01	1,96	2,69
133	0,129	0,131	0,128	1,25	2,08	2,77

\*) not measurable, because G3 was less then 0.100

The results given in table 3 clearly show, that the materials of the present invention, containing emulsions with a high iridium content exhibit a lower Dmin and a higher G3 then emulsions with less iridium and therefore are particularly suitable for digital exposure.

The sensitometric changes on storage of the layer assemblies are summarized in table 4.



Table 4:

Layer assembly	$\Delta D_{min}$			$\Delta G3$		
	Y	M	C	Y	M	C
111	0,045	0,053	0,044	**)	**)	**)
112	0,037	0,048	0,029	**)	-0,93	-0,36
113	0,020	0,035	0,025	-0,22	-0,78	-0,32
121	0,072	0,064	0,026	**)	**)	-0,46
122	0,060	0,033	0,017	**)	-0,95	-0,29
123	0,035	0,020	0,015	**)	-0,83	-0,20
131	0,200	0,158	0,063	**)	**)	**)
132	0,083	0,087	0,041	**)	-0,97	-0,56
133	0,058	0,059	0,035	**)	-0,93	-0,36

\*\* ) not measurable, because G3 was less then 0.100 after storage.

5 The results given in table 3 clearly show, that the materials of the present invention, containing emulsions with a high iridium content exhibit a better storage stability, that is especially pronounced for supports that contain additives like plastizisers.

#### 10 EXAMPLE 10

Layer assembly 200 consisted only of support A.

#### IMAGE QUALITY AND DEFORMATION TEST

15

Layer assemblies 111 to 113, 121 to 123 and 131 to 133 were digitally exposed as described above with an image comprising black characters of varying size (height 3 mm to 10 mm) and chemical processed as described for EXAMPLES 1 to 9.

20 On layer assembly 200 an image comprising black characters of varying size (height 3 mm to 10 mm) was produced by conventional offset printing.

25 A transparent PVC sheet of 80  $\mu$ m precoated on one side with a polyethylene sheet 75  $\mu$ m thick was laid onto the thus prepared image and laminated with the polyethylene in contact with the topcoat of the image layer of layer assemblies 111 to 113; 121 to 123, 131 to 133 and 200. A roller laminator was used for pressing together the superposed materials at a temperature of 104°C measured within the sandwich.

After lamination the following deformation test was applied to layer assemblies 111 to 113, 121 to 123, 131 to 133 and 200. A membrane press was used to press the photographic material onto a work-piece that was pretreated with a wood glue and the test was  
5 run at a temperature of 95°C. The work-piece in the form of a drawer-front was made of chip-wood and had grooves in the form of half-pipes on its front, the half-pipes having a diameter of 0.8 cm. On deformation, the photographic material lying over the halfpipes is pressed in the halfpipe and thereby stretched. The  
10 material is also stretched at the front edges and cornes of the work-piece. At the back-side of the work-piece, overhanging material is cut off. The test pieces were evaluated qualitatively with the following results:

#### 15 DEFORMATION RESULTS

Layer assemblies 111 to 113, 131 to 133 and 200 could easily be deformed and exhibited neither cracks nor micro-cracks.

Layer assemblies 121 to 123 could be deformed, but needed  
20 longer then the layer assemblies mentioned before; they exhibited neither cracks nor micro-cracks.

#### IMAGE QUALITY RESULTS

25 The image quality was evaluated with the naked eye by looking at the black characters in the deformed part of the test pieces. Layer assemblies 111 to 113 and 131 to 133 showed no loss in image quality at the deformed parts.

Layer assemblies 121 to 123 showed minor losses in image  
30 quality that were barely visible as a small loss in density (dark grey instead of black) of the characters in the deformed parts. Layer assembly 200 showed a significant loss in image quality in form of a clearly visible brightening of the characters in the deformed parts. Along the edges and corners grey and even white  
35 lines appear within the characters.

From the test results it is evident, that PVC and PC are preferred supports for the photographic material of the present invention, PVC containing no plastizisers being particularly preferred. The  
40 advantage of PVC is it's ease of deformation and thereby enabling a very smooth deformation that does not at all adversely effect the image quality of the deformed image. The offset printed material

(layer assembly 200) gave a poor image quality upon deformation and cannot be used according to the present invention.

The present invention may include any feature or combination of  
s features disclosed herein either implicitly or explicitly or any  
generalisation thereof irrespective of whether it relates to the  
presently claimed invention. In view of the foregoing description  
it will be evident to a person skilled in the art that various  
modifications may be made within the scope of the invention.

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## CLAIMS

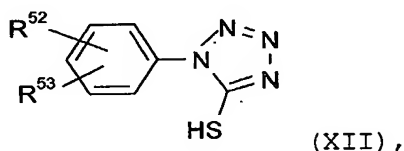
1. A deformable colour photographic silver halide material, said colour photographic silver halide material comprising on a deformable plastic support at least one blue-sensitive silver halide emulsion layer containing at least one yellow coupler, at least one green-sensitive silver halide emulsion layer containing at least one magenta coupler and at least one red-sensitive silver halide emulsion layer containing at least one cyan coupler, wherein the silver halide emulsions have an overall silver chloride content of at least 95 mol% and at least one silver halide emulsion contains silver halide crystals that are doped with 10 to 700 nmol iridium.
2. Material according to claim 1, wherein at least one silver halide emulsion contains silver halide crystals that are doped with 10 to 500 nmol iridium.
3. Material according to claim 2, wherein the silver halide emulsions have an overall silver chloride content of at least 98 mol%.
4. Material according to claim 1, wherein the silver halide crystals of at least one silver halide emulsion contains structured crystals with at least two different zones, the outermost zone having a higher molar content of silver bromide than the rest of the crystal.
5. Material according to claim 1, wherein said support is provided with a subbing layer comprising 1.3 to 80% by weight of a proteinaceous colloid, 0 to 85% by weight of colloidal silica and 0 to 30% by weight of a siloxane, which can form a reaction product with said colloidal silica.
6. Material according to claim 5, wherein said subbing layer is provided on the same side of said support as the silver halide emulsion layers.
7. Material according to claim 1, wherein said green-sensitive silver halide emulsion layer and/or said red-sensitive silver halide emulsion layer contain a silver halide emulsion with

silver halide crystals having an average grain size of at least 0.4  $\mu\text{m}$ .

8. Material according to claim 1, wherein said silver halide emulsion layers contain one or more binders.

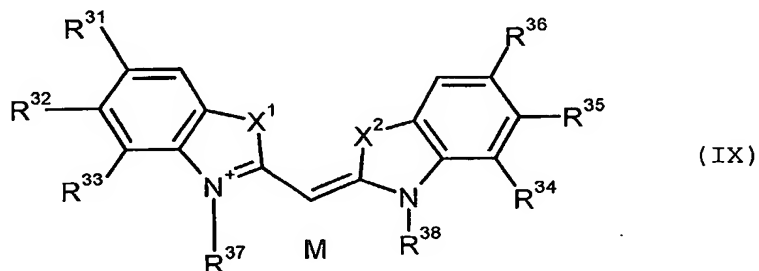
9. Material according to claim 8, wherein said binders in said silver halide emulsion layers are at least 80% by weight gelatin.

10. Material according to claim 1, wherein said colour photographic material contains at least one light-sensitive layer containing a compound represented by formula (XII):



in which  $R^{52}$  represents H,  $\text{CH}_3$  or  $\text{OCH}_3$ ;  $R^{53}$  represents H, OH,  $\text{CH}_3$ ,  $\text{OCH}_3$ ,  $\text{NHCO-R}^{54}$ ,  $\text{COOR}^{54}$ ,  $\text{SO}_2\text{NH}_2$ ,  $\text{NHCONH}_2$  or  $\text{NHCONH-CH}_3$ ; and  $R^{54}$  represents  $\text{C}_1\text{-C}_4\text{-Alkyl}$ .

11. Material according to claim 1, wherein said blue-sensitive silver halide emulsion layer contains a blue sensitizer represented by formula (IX):



wherein  $X^1$  and  $X^2$  independently represent S or Se,  $R^{31}$  to  $R^{36}$  independently represent hydrogen, halogen or an alkyl-, alkoxy, aryl or hetero-aryl group or  $R^{31}$  and  $R^{32}$ ;  $R^{32}$  and  $R^{33}$ ;  $R^{34}$  and  $R^{35}$ ;  $R^{35}$  and  $R^{36}$  together represent the atoms necessary to form an anellated benzo-, naphtho- or heterocyclic ring,  $R^{37}$  and  $R^{38}$  independently represent an alkyl-, sulfoalkyl-, carboxyalkyl-,  $(\text{CH}_2)_1\text{SO}_2\text{R}^{39}\text{SO}_2\text{-alkyl}$ ,  $(\text{CH}_2)_1\text{SO}_2\text{R}^{39}\text{CO-alkyl}$ ,  $(\text{CH}_2)_1\text{COR}^{39}\text{SO}_2\text{-}$

alkyl or  $-(CH_2)_1-COR^{39}CO$ -alkyl group,  $R^{39}$  represents  $-N^-$ - or  $-NH-$ , 1 is a whole number between 1 and 6 and M is an optional counter-ion providing charge compensation.

- s 12. Material according to claim 1, wherein said deformable plastic support is a polycarbonate, poly(vinylchloride), vinylchloride copolymer or a polyester; or a copolyester based on PET.
- 10 13. Material according to claim 1, wherein the outermost layer on the image side of said colour photographic material is provided with a protective foil.
14. A process for producing a deformed image comprising the steps of: exposing the colour photographic silver halide material  
15 according to claim 1; conventionally processing said exposed colour photographic material to produce an image; and deforming said colour photographic material.
15. Process according to claim 14, wherein said deforming step  
20 comprises the application of heat and pressure and wherein at least part of the material is elongated.
16. Process according to claim 14, wherein said deforming step  
25 comprises deforming said deformable colour photographic material in contact with a work piece.
17. Process according to claim 14, wherein said deformable colour photographic silver halide material is provided with a protective foil before deforming said colour photographic  
30 material with a work piece.
18. Process according to claim 14, wherein said deforming step comprises deforming said colour photographic material by vacuum deformation.
- 35 19. Process according to claim 14, wherein said deforming step comprises deforming said colour photographic material by injection moulding.

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## ABSTRACT

## DEFORMABLE COLOUR PHOTOGRAPHIC SILVER HALIDE MATERIAL

5 A deformable colour photographic silver halide material, said  
colour photographic silver halide material comprising on a  
deformable plastic support at least one blue-sensitive silver  
halide emulsion layer containing at least one yellow coupler, at  
least one green-sensitive silver halide emulsion layer containing  
10 at least one magenta coupler and at least one red-sensitive silver  
halide emulsion layer containing at least one cyan coupler, wherein  
the silver halide emulsions have an overall silver chloride content  
of at least 95 mol% and at least one silver halide emulsion  
contains silver halide crystals that are doped with 10 to 700 nmol  
15 iridium

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